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AICE* SURVEY OF USSR AIR POLLUTION LITERATURE

Volume XVIII

PURIFICATION OF GASES THROUGH HIGH TEMPERATURE REMOVAL OF SULFUR COMPOUNDS

Edited By

M. Y. Nuttonson

The material presented here is part of a survey of
USSR literature on air pollution
conducted by the Air Pollution Section
AMERICAN INSTITUTE OF CROP ECOLOGY

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3 CZECHOSLOVAKIA—Agricultural Climatology of Czechoslovakia and Its Agro-Climatic Analogues in North America

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PREFACE

The present volume represents a translation of a Russian monograph* intended for a broad segment of engineers, technicians, and scientists in the chemical, power, gas, coal, and metallurgical industries. In the introduction to the monograph the authors state that in recent years the problem of recovery of sulfur compounds from industrial waste gases has become highly important in the area of sanitary protection of atmospheric air. They point out that sulfur dioxide discharged into the atmosphere together with the waste gases is harmful to the health of the population, damages vegetation, and has a corrosive effect on buildings and installations.

The monograph presents the results of the authors' numerous theoretical and experimental studies which deal with the removal of sulfur compounds (hydrogen sulfide and sulfur dioxide) from heated gaseous mixtures through the use of dry methods and without lowering the temperature of the gases.

The authors discuss problems of selection of solid reactants suitable for the removal of hydrogen sulfide gases at 500-1100°C., and also for the removal of sulfurous anhydride at 400-800°C. Results of performed thermodynamic and numerous experimental studies are given. Conditions of processes of high-temperature purification of gases by means of solid reagents are indicated. Prospects for the use of dry methods of removal of sulfur compounds from gases at high temperatures under conditions of combustion of sulfur fuels at steam power plants are evaluated.

It is hoped that the monograph selected for presentation in this volume will be conducive to a better appreciation of some of the air pollution investigations conducted in the USSR. As the editor of this volume I wish to thank my co-workers in the Air Pollution Section of the Institute for their valuable assistance.

M. Y. Nuttonson

November 1972

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* "Vysokotemperaturnaya Ochistka Gazov ot Sernistykh Soedineniy". (Purification of Gases Through High Temperature Removal of Sulfur Compounds.) V. S. Al'tshuler, A. A. Gavrilova. Akademiya Nauk SSSR. Ministerstvo Ugol'noy Promyshlennosti SSSR. Institut Goryuchikh Iskopaemykh. Izdatel'stvo "Nauka", Moskva, 148 pages, (1969).

INTRODUCTION

The extraction of sulfur components from gaseous mixtures is an important technological process, very common in modern technology. The use of this process is determined by purely technological needs and by the stringent limitations connected with the sanitary protection of the purity of the air reservoir. In industry, purification of gases involving removal of sulfur compounds is required in many cases in order to ensure a normal course of the main production process. For example, the presence of sulfur in gases used for the synthesis of ammonia, methanol, and other organic compounds causes poisoning of the catalysts and brings the process to a standstill. For this reason, the gas should be thoroughly purified by removing all the sulfur compounds.

Nearly all combustible gases used for the production of power and for technological purposes are subjected to purification involving removal of sulfur compounds. Many years of experience have shown that in all cases, the purification improves the quality of the gas, facilitates the conditions of its utilization and extends the scope of its application.

In recent years, in the USSR and almost everywhere else in the world, a special importance has been assumed by the problem of recovery of sulfur compounds from industrial waste gases, chiefly in the area of sanitary protection of atmospheric air. The sulfur dioxide discharged into the atmosphere together with the waste gases is harmful to the health of the population, damages the vegetation, and has a corrosive effect on buildings and installations.

The chief source of contamination of the air reservoir with sulfur dioxide are the flue gases of fuel-burning power installations, primarily, major thermal electric power plants operating on sulfur-containing fuels (mazuts, coal, and others). It has been calculated, for example, that since the time when mankind began to burn sulfur mazuts and coal, about 10% of the world output of metal has been expended in compensating for the losses due to corrosion.

Considerable damage is also caused by sulfur-containing waste gases of nonferrous metallurgy (copper- and nickel-smelting plants), sulfuric acid production, etc. A large number of methods have been proposed for removing various sulfur compounds (hydrogen sulfide, sulfur dioxide, organosulfur compounds) from gases, i.e., methods that have been used in an enormous amount of research and experimental industrial work. In describing the industrial development of these methods, one can note the broad industrial application of methods of purification of gases involving only the removal of hydrogen sulfide and organic sulfur.

A large number of major installations removing hydrogen sulfide and organosulfur compounds from gases by different purification methods, primarily liquid ones, are operating in the chemical and other industries according to the composition and amount of the gas being purified and the degree of purification required. Here the removal of sulfur compounds from gases is an important part of the technological setup of the entire industry, and in most cases involves utilization of the recovered sulfur in the production of commercial goods.

The situation is much worse in the case of industrial development of methods of sulfur dioxide removal from gases. Despite the large number of studies made on the removal of sulfur dioxide from gases, their results cannot be considered adequate for industrial utilization on the necessary scale. Actually, there are as yet no processes applicable to large-scale industrial purposes that would permit an economical extraction of sulfur dioxide from waste gases.

For this reason, the problem of preventing the discharge of harmful sulfur-containing gases into the atmosphere is very serious for many branches of the national economy, primarily for thermal electric power plants. The chief difficulties in the creation of efficient and economical methods of removal of sulfur dioxide from the flue gases of electric power plants lie, on the one hand, in the large volumes of gases subjected to purification (8000 m^3 per ton of reference fuel) and, on the other hand, in the small concentrations of sulfur dioxide in the gases (0.1-0.4% by volume). The presence of mechanical particles (soot, ash) in the flue gases also complicates their purification.

The inadequacy, mainly from the standpoint of technical and economic considerations, of the methods of purification of flue gases proposed thus far has been responsible for the tendency to use high smokestacks in meeting the sanitary requirements in modern thermal power engineering. In this case, the atmospheric concentration of noxious sulfur compounds which is allowed by sanitary requirements is achieved mainly by increasing the dispersing capacity of the smokestacks or limiting the output of electric power plants when the dispersing capacity of the stacks has reached its limit.

However, even though the dispersal of pollutants over large areas and volumes decreases their concentration, the total discharges into the atmosphere are not decreased, and their noxious effect on the environment remains, being only slowed down in time. All this confirms the fundamental inadequacy of the existing measures for controlling the pollution of the air reservoir, particularly in connection with the considerable growth of the unit capacities of electric power plants, and also in light of the social requirements of complete elimination of the noxious effects of the discharges.

A graphic description of the method of controlling noxious impurities by increasing the dispersing capacity of smokestacks may be formulated as follows: "the higher the stack, the lower and weaker the science". More desirable and justified is not the dispersal of sulfur dioxide, but the prevention of its appearance in the gases being emitted through a smokestack. This may be achieved not only by creating new, efficient methods of purification of flue gases, but also by removing the sulfur at the stage of preparation of the fuel for combustion.

In thermal power engineering great interest has been shown in recent years in solving the problem of recovery of sulfur by first gasifying the sulfur fuel. This trend specifies a residue-free gasification of the organic part of the fuel, removal of sulfur compounds from the gas obtained, and its subsequent use in power production. In this case, the boiler unit is not exposed to the action of sulfur gases and their mechanical impurities, and the amount of gases being subjected to purification is about one-half as much as in the case of purification of flue gases.

The most important condition for the use of gasification in the removal of sulfur as a stage of preparation of sulfur fuel for combustion is the achievement of a high energy efficiency of the entire process. Essentially, this problem consists in a maximum decrease of the fuel loss in the main process of gas generation and in the preservation of the physical heat from the hot combustible gases obtained during their purification involving removal of sulfur and other undesirable impurities before they are supplied to the power plant. The decrease of direct fuel loss during gasification is determined by the characteristics of the gas-generating process. On the whole, it may be assumed that in gasification, this loss will be equal to that resulting from incomplete combustion (carryover, loss with slag) during the direct combustion of the corresponding fuels. Therefore, from this standpoint, the inclusion of the fuel gasification process in the scheme of an electric power plant will have little effect on the heat economy of electric power production.

A more substantial influence on the efficiency of the process may be exerted by the stage of removal of sulfur compounds from the gases, and particularly the removal of hydrogen sulfide, which during gasification is the chief sulfur-containing component of the gas obtained. The methods of removal of hydrogen sulfide from gases used thus far are carried out at low temperatures and require considerable cooling (down to 100°C) with an appreciable loss of physical heat and expenditure of energy on purification and cooling, resulting in a decrease of the energy efficiency. Within certain limits, this decrease may be offset by cooling the gases in waste heat boilers, which are included as an element of the thermal electric power plant. However, even in this case, when low-temperature gas purification is used, one must not neglect a certain drop of the total energy efficiency of the electric power plant. Thus a major importance is acquired by the creation of dry, high-temperature methods of removal of hydrogen sulfide from gases, the use of which would permit the preparation of the fuel without any appreciable heat loss.

This monograph gives a survey of studies made in this area and presents the results of theoretical and experimental research conducted by the authors on the high-temperature purification of gases involving removal of hydrogen sulfide. Considering certain prospects of creating dry, high-temperature methods of gas purification with the removal of sulfur dioxide as well, the monograph classifies the existing material and gives the results of the authors' studies of this subject. Accordingly, the monograph consists of two main parts: 1) removal of hydrogen sulfide and 2) removal of sulfur dioxide from gases.

The authors take this opportunity to express their gratitude to M. I. Nedashkovskaya, G. F. Dushin and O. Ye. Vol'naya, on the staff of the laboratory of gas processes at the Institute of Mineral Fuels for their assistance in the compilation of the monograph, and to K. T. Ostrikovaya for putting it in final shape.

I

REMOVAL OF HYDROGEN SULFIDE FROM GASES

Review of the Processes and Methods of Removal of Hydrogen Sulfide from Gases

The process of removal of hydrogen sulfide from gases is widely used in various branches of industry - chemical, gas, petrochemical, and others. This process has been used in gas technology for a long time, since the start of the last century, and historically was first developed in urban illuminating-gas plants. Later, hydrogen sulfide began to be removed from gases of the coke industry, natural and technological gases, synthesis gases, and hydrogen.

Initial proposals concerning the removal of hydrogen sulfide from gases involved its absorption by various absorbents in solid fragments at moderate temperatures. Processes using slaked lime, iron hydroxide, natural bog ore and others were applied in industry.

For many years thereafter, the development of the processes of removal of hydrogen sulfide from gases amounted to many proposals concerning the composition of the absorbents and to the improvement of the technology of the processes involving their use.

A definite breakthrough in the development of the technology of removal of hydrogen sulfide from gases occurred in the 1930's in connection with the development in 1921 in the U.S.A. of the so-called Seabord process, based on the use of an absorbent soda solution.

Since that period until the present time, the removal of hydrogen sulfide from gases evolved in the direction of the creation and development mainly of liquid (wet) methods of purification. Liquid processes did not displace dry ones, which continue to develop, since they have many advantages, for example, a higher degree of purification.

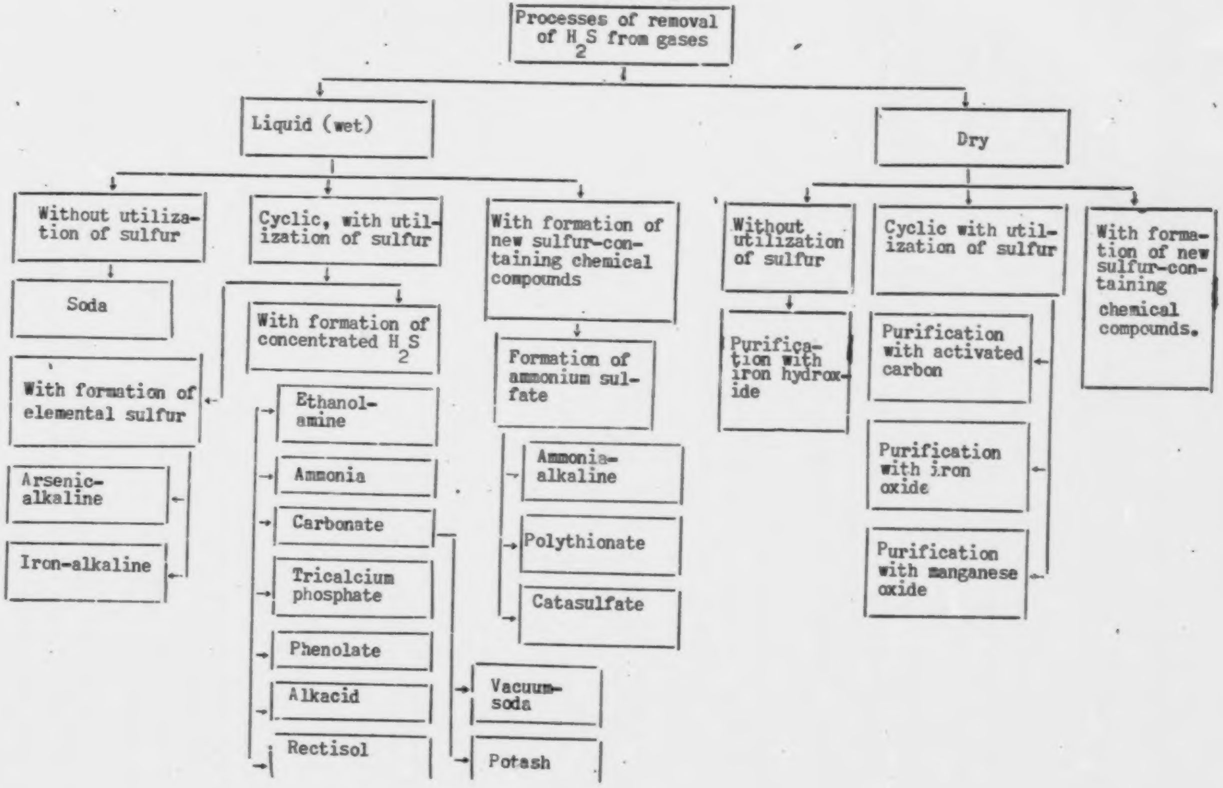
A classification of the liquid and dry processes is given in flow chart 1.

According to the characteristics of the conditions of utilization of the hydrogen sulfide being recovered, three groups can be distinguished in each of these processes. The first group includes processes and methods whose main purpose is only gas purification, without utilization of the hydrogen sulfide being recovered.

The products of the main reaction of hydrogen sulfide with any given reactants are the waste in this case and are discarded. In the category of liquid processes, this group includes the above-mentioned soda ("Seabord") process based on the reaction

$$Na_2CO_3 + H_2S \rightleftarrows NaHS + NaHCO_3.$$

Technological flow chart 1. Classification of processes of removal of hydrogen sulfide from gases.


Processes of removal of H_2S from gases
Liquid (wet)
Dry
Without utilization of sulfur
Cyclic, with utilization of sulfur
With formation of new sulfur-containing chemical compounds
Without utilization of sulfur
Cyclic with utilization of sulfur
With formation of new sulfur-containing chemical compounds.
Soda
With formation of elemental sulfur
Arsenic-alkaline
Iron-alkaline
With formation of concentrated H_2S
Ethanolamine
Ammonia
Carbonate
Tricalcium phosphate
Phenolate
Alkacid
Rectisol
Vacuum-soda
Potash
Formation of ammonium sulfate
Ammonia-alkaline
Polythionate
Catasulfate
Purification with iron hydroxide
Purification with activated carbon
Purification with iron oxide
Purification with manganese oxide

This process consists in the absorption of hydrogen sulfide in a dilute solution of sodium carbonate (≈1-3.5%) at 35°C., followed by regeneration the solution by bubbling air, which carries away the hydrogen sulfide and is discharged into the atmosphere. An example of a dry process can be the absorption of hydrogen sulfide by iron hydroxide under conditions where the spent mass is characterized by a relatively low sulfur content.

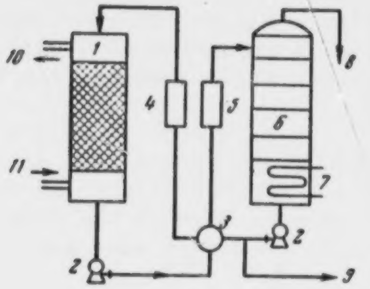


Fig. 1. Flow chart of liquid cyclic processes.

1 - gas washer; 2 - pump; 3 - heat exchange; 4 - cooler; 5 - heater; 6 - distillation column; 7 - boiler; 8 - exit of acid gases; 9 - exit of fresh solution; 10 - exit of purified gas; 11 - entrance of unpurified gas.

The low efficiency of the processes of gas purification without utilization of sulfur and the serious sanitary limitations on the discharge of sulfur-containing products (hydrogen sulfide into the atmosphere and the absorbent mass into dumps) make such processes unsuitable for broad industrial application.

The second group includes the so-called cyclic processes and methods by which either commercial hydrogen sulfide or elemental sulfur is obtained. Here hydrogen sulfide is recovered from the gases by means of reactants which are subjected to regeneration and are recycled for subsequent reuse.

A flow chart of liquid cyclic processes for recovering hydrogen sulfide is shown in Fig. 1. The main units of this scheme are an absorber and a desorber, the designs of which may be of different types: packed, bubbling, and others. In addition, depending on the composition of the absorber, purpose of the unit and conditions of its operation, additional special devices and installations are introduced into the scheme. Various solutions have found applications as absorbers in liquid cyclic processes: alkaline-arsenic, ethanolamines, acid carbonates (soda, potash), ammonia, and other solutions. Regeneration of the absorbers in liquid cyclic processes is accomplished by decreasing the pressure, heating the solution, and blowing air or water vapor through it.

Hydrogen sulfide recovered from gases in cyclic liquids and dry processes may be subjected to oxidation directly in the course of purification with formation of elemental sulfur, or isolated during regeneration of the absorbent in concentrated form for further use.

In processes of gas purification involving removal of hydrogen sulfide with formation of elemental sulfur, the chief end result is the reaction

$$H_2S + 0{,}5O_2 \rightleftarrows H_2O + S.$$

Dry oxidation processes with formation of elemental sulfur, based on this reaction, will be discussed below. In order to ensure the oxidation of hydrogen sulfide to elemental sulfur, use is made in liquid processes of alkaline solutions containing chemicals which enter into irreversible chemical reactions with hydrogen sulfide.

Among such cyclic liquid processes, the arsenic-soda process (the so-called Phylox process) has been most widely applied. Without discussing the mechanism of this process, which has been closely studied both in the USSR [1] and abroad, one can note that the determining reactions in this case are

$$Na_4As_2S_5O_2 + H_2S \rightarrow Na_4As_2S_6O + H_2O,$$
$$Na_4As_2S_6O + 0{,}5O_2 \rightarrow Na_4As_2S_5O_2 + S.$$

Similar determining reactions may take place in the iron-soda process ("ferrox" process), iron-cyanide processes, and others.

The regeneration of absorbing solutions in all these processes is usually carried out by blowing air through them, so that sulfur is replaced by oxygen in the molecule of the absorbing reactant, sulfur precipitates out in finely divided form, and is floated with air. It is essential to note that in processes where the reactants used are suspensions instead of not readily soluble substances (iron-alkaline and iron-cyanide processes), the sulfur obtained is highly contaminated with the solid reactant, something that does not occur in the purification of gases by the arsenic-soda process. The absorbent solutions used in the purification of gases in this group of processes are usually characterized by a low concentration of the main reactants, this being due to the regeneration conditions of the solutions. Their sulfur capacity, i. e., the amount of hydrogen sulfide which can be absorbed by 1 m^3 of solution, is 1.5 kg. For this reason, the absorption process makes it necessary to use considerable amounts of absorbent solutions.

An important characteristic of the process is the degree of development of side reactions. When alkaline solutions of reactants are used, not all of the absorbed hydrogen sulfide is converted into sulfur. Part of it enters into a side reaction with the formation of thiosulfate, so that it is removed from the cycle together with part of the absorbing solution. According to actual data, about 10-20% of the sulfur absorbed from the gas by the arsenic-soda solution oxidizes to hyposulfite during regeneration of the solution. In iron-alkaline processes, up to 30-40% of the weight of absorbed sulfur is converted into hyposulfite. Let us note in passing that attempts to modify the iron-alkaline processes by replacing iron with nickel or copper have not been applied in industry. A technological flow chart of the assembly for the removal of hydrogen sulfide from gases by the process most commonly used, the arsenic-soda process, with formation of elemental sulfur, is shown in Fig. 2. This purification process is selective, i. e., there is a high selectivity for hydrogen sulfide. The presence of carbon dioxide, even in amounts up to 20%, has no appreciable effect on the process of hydrogen sulfide recovery.

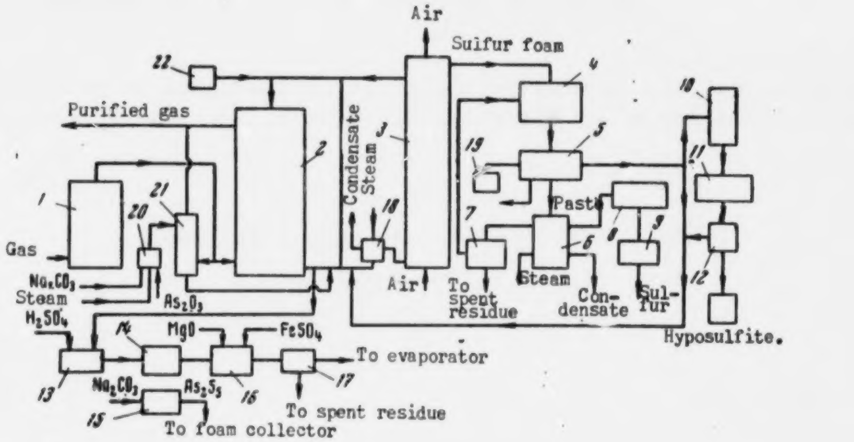

Air
Sulfur foam
22
4
18
Purified gas
2
Condensate
Steam
3
5
19
11
1
21
Paste
20
18
7
8
9
Gas
6
Na₂CO₃
Steam
As₂O₃
Air
To spent residue
Steam
Con-densate
Sul-fur
12
H₂SO₄
14
MgO
FeSO₄
Hyposulfite.
To evaporator
13
Na₂CO₃
As₂S₅
16
17
15
To spent residue
To foam collector

Fig. 2. Technicological flow chart of assembly for the removal of hydrogen sulfide from gases by the arsenic-soda process.

1 - electrostatic precipitator; 2 - absorber; 3 - regenerator; 4 - foam collector; 5 - vacuum filter; 6 - autoclave; 7 - settling tank for autoclave liquid; 8 - liquid-sulfur collector; 9 - cooling drum (or pan); 10 - evaporator; 11 - crystallizer; 12 - centrifuge; 13 - first-stage neutralizer; 14 - neutralization vacuum filter; 15 - solvent for arsenic sulfide; 16 - second-stage neutralizer; 17 - filter press or settling tank; 18 - solution heater; 19 - unit for obtaining colloidal sulfur; 20 - solvent for Al_2O_3; 21 - saturation scrubber; 22 - tank for soda solution.

Among the liquid cyclic processes of removal of hydrogen sulfide from gases with formation of elemental sulfur, one can also include a process using sulfur dioxide. This process is based on the reaction of H_2S with SO_2 in aqueous solutions with the precipitation of sulfur.

$$2H_2S + SO_2 = 3S + 2H_2O.$$

Detailed studies have established that a considerable part of the sulfur does not precipitate in the free form, but is used up in the formation of thiosulfate, polythionates and thioacids. The impossibility of controlling the course of these reactions, an intensive corrosion of the equipment, and also a low rate of the main reaction have caused work on this process to be virtually discontinued.

Cyclic processes involving formation of concentrated hydrogen sulfide, based on a physicochemical equilibrium and the reversibility of the absorption reaction and evolution of hydrogen sulfide have become highly popular in gas purification techniques.

In such liquid processes, absorption of hydrogen sulfide from gases is accomplished with the aid of solutions of weak bases (amino derivatives) or salts of strong bases and weak acids (phenolates, phosphates, soda, and others). The absorption process is carried out at a low temperature, about 35°C.

The main reaction underlying the proposed processes of sulfur purification with formation of concentrated hydrogen sulfide may be expressed as follows:

Ethanolamine Process

$2RNH_2 + H_2S \rightleftarrows (RNH_3)_2S$ - monoethanolamine (MEA) process,

$2R_2NH_2 + H_2S \rightleftarrows (R_2NH_2)_2S$ - diethanolamine (DEA) process,

$2R_3N + H_2S \rightleftarrows (R_3NH)_2S$ - triethanolamine (TEA) process.

where $R = CH_2CH_2OH$.

Phenolate Process

$$C_6H_5ONa + H_2S \rightleftarrows C_6H_5OH + NaHS$$

Phosphate Process

$$K_3PO_4 + H_2S \rightleftarrows K_2HPO_4 + KHS,$$

$$K_2HPO_4 + H_2S \rightleftarrows KH_2PO_4 + KHS.$$

Carbonate Process

$Na_2CO_3 + H_2S \rightleftarrows NaHS + NaHCO_3$ - vacuum-soda process

$K_2CO_3 + H_2S \rightleftarrows KHS + KHCO_3$ - potash process.

Alkacid Process

$$R'COOK + H_2S \rightleftarrows R'COOH + KHS,$$

where R' os $(CH_3)_2\ N\text{-}CH_2\text{-}$ (radical of alkacid DIA).

The regeneration of the absorbing solutions is usually carried out by heating them to boiling. As a result of the temperature elevation, the solubility of hydrogen sulfide decreases, the hydrolysis of its salts with weak bases (amino derivatives) increases, and the volatile hydrogen sulfide is displaced from solutions of weak acids of low volatility. Thus the equilibrium partial pressure of hydrogen sulfide above the solution is considerably increased, and this gas is driven off together with water vapor. The concentrated hydrogen sulfide obtained after the condensation of water vapor is then used to produce sulfur or sulfuric acid.

The absorbing solutions (usually of high concentration) used in this group of processes have a high sulfur capacity, up to 65 kg of hydrogen sulfide per m^3 of solution, and for this reason a relatively small amount of the latter is kept in circulation.

The equipment of the individual liquid cyclic processes of gas purification with formation of concentrated hydrogen sulfide is very similar and differs only in the absorbing reactant used. To give a general representation of the technological design of such processes, Fig. 3 shows a diagram of an assembly for the process with monoethanolamine purification. Among the cyclic processes of the second group one can also include the process of so-called Rectisol purification, based on the absorption of hydrogen sulfide with methanol cooled down to the range of -30 to -70°C. at pressures from 5 to 50 atm. In this process, methanol acts only as the solvent, without entering into intermediate chemical compounds with the gas being absorbed.

The third group of processes of gas purification involving removal of hydrogen sulfide is characterized by the fact that the extraction of hydrogen sulfide is carried out in a single complex that is used to produce new chemical compounds. Here the gas purification is associated with the synthesis of by-products whose value frequently determines the general desirability of carrying out the given process. The absorbents most frequently used are chemicals that simultaneously absorb hydrogen sulfide (under conditions of its oxidation) and ammonia to produce ammonium sulfate. Such processes have been developed chiefly for the purpose of removing hydrogen sulfide from coke-oven gas and simultaneously extracting ammonia. Of the processes proposed for this purpose (Fel'd's polythionate process, Burkheiser's sulfite-bisulfite process and others), the most interesting is the "catasulf" process, based on the catalytic oxidation of hydrogen sulfide with oxygen in the presence of other combustible gases to sulfur dioxide, and the absorption of NH_3 and SO_2 by sulfite liquors. The ammonium bisulfite and ammonium sulfite obtained are then oxidized to the sulfate.

However, despite the large number of studies made in this area, this process has not been developed in industry, chiefly because of its technological complexity, considerable corrosion of the equipment, and dependence of the course of the process on the ratio of ammonia to hydrogen sulfide concentrations in the gas.

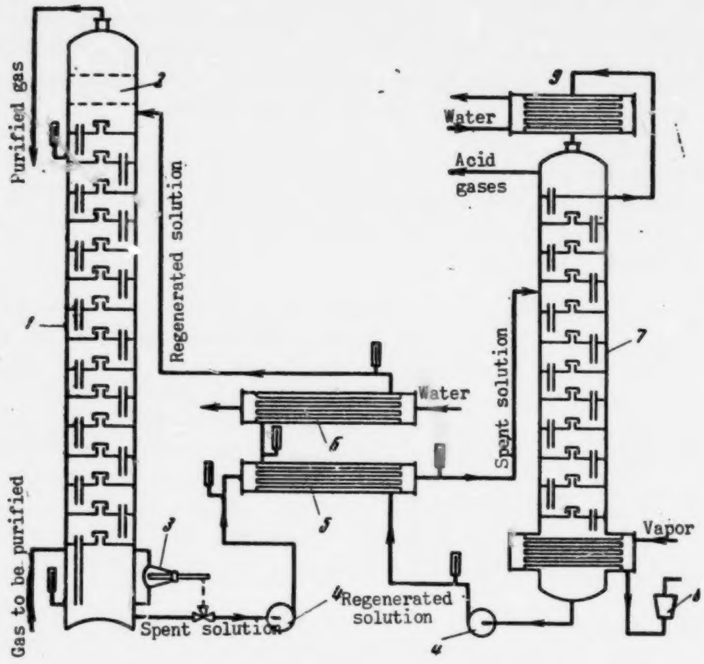

Purified gas
2
Regenerated solution
1
Gas to be purified
3
Spent solution
4
Regenerated solution
4
Water
6
5
Spent solution
9
Water
Acid gases
7
Vapor
8

Fig. 3. Flow diagram of gas purification assembly using the ethanolamine process.

1 - absorber; 2 - trap; 3 - level controller; 4 - pump; 5 - heat exchanger; 6 - cooler; 7 - regenerator; 8 - condensation vessel; 9 - dephlegmator.

The above brief review of the three groups of processes differing in the conditions of utilization of the recovered sulfur must not be considered as a complete characterization of the existing processes of removal of hydrogen sulfide from gases. The majority of these processes have been described in detail in specialized literature [2-5]. For this reason, we shall hereinafter dwell only on some general aspects of hydrogen sulfide removal from gases with reference to the stated problem, i. e., high-temperature gas purification. Obviously, primary attention should be focused in this case on the characteristics of dry purification methods.

The variety of the processes of hydrogen sulfide removal from gases proposed up to the present time is not accidental and cannot be accounted for solely be the natural development of gas engineering. Apparently, this is largely due to the variety of the specific conditions under which the removal of sulfur from gases had to be carried out. Depending on the purpose and degree of gas purification desired, composition of the initial gas, output of the installations, possibility of utilizing the recovered sulfur, pressure, sipply of raw material for the preparation of absorbents, and other factors, different requirements have appeared with regard to the gas purification process, and thus certain other processes were created. It is therefore very difficult to compare the technical-economic indices according to the existing methods of sulfur removal, since these indices, even for the same method and a given output, fluctuate over wide limits depending on many of the abovementioned factors.

Nevertheless, as a general argument on the efficiency of gas purification processes, it may be noted that the magnitude of capital investment in all the processes is determined by the gas load and is independent of the sulfur content of the gas. As far as the operational cost and expenditure indices are directly proportional to the amount of sulfur being recovered from the gas. Hence it may be concluded that in the purification of gases with a low hydrogen sulfide content, particularly in the case of purification of power plant gases, the dry gas purification processes will be more competitive.

Of major importance for ensuring an efficient purification of gases is the composition of the gas mixture undergoing purification. For example, cyclic processes in which the carbonates formed are not decomposed during regeneration are not suited for gases containing carbon dioxide. Among liquid processes, this applies to the phenolate and phosphate ones. Some liquid processes, for example, the ethanolamine and alkacid ones, can be used independently for the absorption of carbon dioxide from gases. In the case of joint absorption of H_2S and CO_2, it is necessary to consider only the corresponding change of the flow coefficients.

The presence of a certain amount of oxygen in the gases being purified is allowed in almost all dry methods of sulfur removal. In cyclic liquid processes, the presence of oxygen in the gases causes the formation of hyposulfite, and this affects the economics of the process (cost and consumption of additional absorbent). As is shown by theory and experiment, in all sulfur removal processes, it is desirable to use a higher pressure in order to achieve a greater efficiency. However, this does not justify the expense involved in compressing the gas if the pressure is used only to improve the sulfur re moval. For this reason, pressure is desirable only in cases where this is dictated by other, technological, considerations.

It is very important to note that almost all of the proposed liquid processes of sulfur removal are carried out at moderate temperatures limited by the boiling points of the absorbent solutions (usually at 30-40°C.).

It is of definite interest to make a comparative evaluation of the various liquid processes of hydrogen sulfide removal from gases in order to consider their characteristics in the development of dry high-temperature processes. Here it should be pointed out first of all that as a result of numerous theoretical and experimental studies, serious industrial objections have been raised to a number of the processes, casting doubt on the desirability of their further development. Thus, for example, in almost all the processes utilizing hydrogen sulfide to produce new chemicals and in oxidation processes involving formation of elemental sulfur (with the exception of arsenic processes), an extensive development of side reactions, a slow rate of the principal reactions, the practical impossibility of maintaining the stoichiometric ratios of the reactants, and a considerable corrosion of the equipment have been established. Arsenic-alkaline processes were found to be more advantageous as compared with iron-alkaline ones in view of the purity of the sulfur obtained.

The indices of cyclic phenolate, phosphate and alkacid processes are clearly inferior to the ethanolamine process of hydrogen sulfide removal from gases. Therefore, it is possible at the present time to discuss the following liquid processes of hydrogen sulfide removal from gases, i. e., processes having industrial importance and prospects for further development: arsenic-alkaline, ethanolamine, carbonate (soda and potash) and Rectisol processes.

From the standpoint of the degree of purification of gases, the best of these processes may be considered to be the ethanolamine process, in which a purification of up to traces of hydrogen sulfide is attainable.

The arsenic process permits a hydrogen sulfide recovery resulting in a residue of 0.1-0.5 g/m^3 in the gas. Carbonate processes give a degree of purification of about 90%. The ethanolamine process also has advantages over other liquid processes in the sulfur capacity of the solution (and hence, a lower consumption of steam) and in the technological simplicity of the process (absence of a vacuum or deep cooling). Among the advantages of the carbonate processes is the use of low-pressure waste steam, a point that must not be disregarded when such processes are used at thermal electric power plants.

As already indicated, all the liquid processes of hydrogen sulfide removal from gases are carried out at moderate temperatures, and therefore even the best of these processes do not meet the requirements of their utilization for purifying hot gases without preliminary cooling.

In reference to the stated objective, i. e., the creation of high-temperature purification processes, of greatest interest are dry processes of hydrogen sulfide removal from gases. The dry gas purification processes are not as numerous as those involving liquid removal of hydrogen sulfide from gases. Two processes have been widely accepted in industry: removal of H_2S from gases by iron oxides and by activated carbon.

Removal of H_2S from gases by iron oxide. This process has been adequately perfected and is carried out at 30°C. In recent years, reports have appeared on the development and industrial verification of this process at 350-400°C. [6]. The low-temperature process consists in passing the gas slowly through the purifying mass, containing ferric hydroxide. The main reactions of this process may be schematically represented by the following equations:

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O,$$
$$2Fe(OH)_3 + H_2S = 2Fe(OH)_2 + S + 2H_2O,$$
$$Fe(OH)_3 + H_2S = FeS + 2H_2O.$$

These reactions are characteristic of the process when an alkaline absorbent mass is used. In the absence of an alkali, the reaction follows the equation

$$2Fe(OH)_3 + 3H_2S = 2FeS + S + 6H_2O.$$

As the gas is gradually passed through the mass, its content of active ferric oxide decreases, the content of the reaction products - ferrous sulfide and sulfur - increases, the reactivity of the mass diminishes, and breakthrough of the unreacted hydrogen sulfide begins.

Regeneration of the spent mass consists in its treatment with a steam-air mixture. As a result, ferrous sulfide is converted back into ferric hydroxide, and elemental sulfur separates out, and remains mixed with the mass, which is ready to react again. This involves the following principal reactions:

$$2Fe_2S_3 + 3O_2 + 6H_2O = 4Fe(OH)_3 + 6S,$$
$$4FeS + 3O_2 + 6H_2O = 4Fe(OH)_3 + 4S.$$

While absorbing hydrogen sulfide from the gas and undergoing regeneration, the gas-purifying mass becomes increasingly enriched with elemental sulfur (practically up to 35-50%) before it is completely spent. The reactivity of such a mass is low, and it is therefore replaced with a fresh one. Both stages - absorption of sulfur and regeneration of the mass - are associated with the evolution of heat. When sulfur is absorbed, the evolution of heat is small, since the concentration of hydrogen sulfide in the gas is low, but this involves evaporation of a small portion of the moisture present in the mass. In regenerating the mass, it is necessary to take special steps to provide for the necessary temperature conditions. The largest amount of sulfur bound by the mass is evaluated from its Fe_2O_3 content, which should be no less than 50%. However, the content of active modifications of ferric oxide (α and γ) is more important in this case.

The first modification (α) is present in bog ore, while the second enters into the composition of red mud, which is the waste from the production of alumina from bauxites. Practice shows that the absorbent mass should have a porosity of 50%. The spent absorbent mass is usually utilized by sulfuric acid plants as a substitute for pyrite in the production of sulfuric acid.

Attempts to isolate sulfur from the spent mass by extraction with carbon disulfide, kerosene and other solvents failed to yield any satisfactory results from the economic standpoint. On the whole, the process of removal of H_2S from a gas by means of ferric oxides at low temperatures is characterized by a high degree of purification of the gas, and also technological simplicity and reliability. Disadvantages of this process include its intermittent character and primarily, the bulk of the equipment, whose large size is due to low reaction rates at moderate temperatures.

These disadvantages are avoided for the most part by carrying out the process at higher temperatures.

A large number of laboratory and experimental industrial studies aimed at developing a process for recovering hydrogen sulfide from gases by means of iron oxides in a stationary and fluidized bed at temperatures up to 400°C. were recently conducted in England with reference to the purification of coke-oven gas [6].

Laboratory experiments on the conditions of the reaction between sulfur coke-oven gas ($H_2S \approx 1\%$) and ferric oxides in a stationary bed were carried out in a quartz tube 25 mm in diameter with particles up to 1 mm in size at a gas velocity of 0.05 m/sec.

At 250° C. and a space velocity of 100 hr^{-1}, and also at 400°C. and a space velocity of 140 hr^{-1}, and almost complete recovery of hydrogen sulfide was achieved. Similar results for the degree of removal of hydrogen sulfide from the gas were obtained by using iron oxides in a fluidized bed in a reaction vessel 5 cm in diameter at 400°C. and a space velocity up to 300 hr^{-1}. Experiments were also carried out on the regeneration of sulfur-containing iron oxides by firing them in a stream of air at a temperature up to 800°C. and checking their activity after the firing. The experiments showed the feasibility of a complete cycle of H_2S removal from the gas by means of ferric oxides at the indicated temperatures, i. e., up to 400°C. On the basis of results of laboratory studies, a semicommercial assembly with an output of 3000 m^3/hr using sulfur-containing coke-oven gas and a fluidized bed of iron oxides at 400°C. was installed at the Appleby-Frodingham plant in 1956. A diagram of the installation is shown in Fig. 4. The operation of this assembly has essentially confirmed the results of laboratory experiments and shown the practical desirability of an industrial application of this process.

Of interest from a theoretical and practical standpoint are studies of the kinetics of the reaction of hydrogen sulfide with ferric oxides at high temperature, conducted by O. P. Korobeynichev [7]. He studied the effect of temperature, pressure, initial composition of the gas phase, space velocity of the gas, particle size, and conditions of pretreatment of the reactant on the course of the reactions of hydrogen sulfide, carbonyl sulfide, and carbon disulfide with iron oxides.

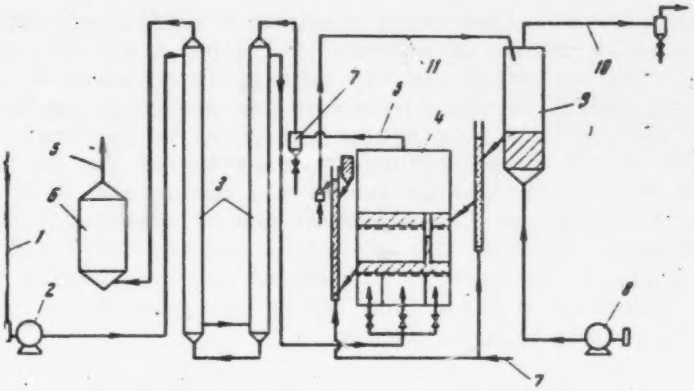


Fig. 4. Diagram of assembly at Appleby-Frodingham.

1 - sulfur-containing gas; 2 - gas blower; 3 - heat exchangers; 4 - two-stage adsorber with fluidized bed; 5 - purified gas; 6 - scrubber; 7 - inert gas; 8 - air blower; 9 - regenerator; 10 - gas enriched with sulfur dioxide; 11 - iron oxides.

The kinetics of this reaction of hydrogen sulfide with iron and its oxides were studied at 150-350°C.

A first order of the reaction with respect to hydrogen sulfide was established together with an accelerating effect of hydrogen and carbon monoxide on the recovery of hydrogen sulfide from the gases.

O. P. Korobeynichev also carried out short-term laboratory experiments to study the course of the process of removal of H_2S from producer gas at temperatures up to 900°C. using Tikhvin bauxites.

The conditions of the process of H_2S removal from gases in a fluidized bed of iron cinder were also studied by M. Altybayev, Yu. I. Savchenko et al. [8]. They confirmed the possibility of achieving a 100% removal of H_2S from gases at 300°C.

Purification of gases with activated carbon. The process is based on the property of activating coals to adsorb hydrogen sulfide and exert a catalytic effect on its oxidation to elemental sulfur. In this process, the gas to be purified, mixed with air necessary for the oxidation, is passed through a bed of activated carbon.

The overall equation of such a process may be expressed as follows:

$$2H_2S + O_2 = 2H_2O + 2S.$$

To make sure that the reaction takes place at a sufficient rate at ordinary temperature, a small amount of ammonia (0.2 g per 1 m^3) is added to the gas being purified. The action of ammonia apparently consists in maintaining the necessary alkalinity of the surface of the activated carbon. The elemental sulfur being produced obliterates the pores of the coal, gradually decreasing its activity and thus limiting the duration of its continuous service. Depending on the characteristics of the coal, from 50 to 150% of sulfur relative to the weight of the adsorbent can be adsorbed before the breakthrough of hydrogen sulfide. The adsorbent is then subjected to regeneration. This stage of the process is carried out by treating the coal with a solution of ammonium sulfide. The latter extracts the sulfur from the pores of the coal, forming polysulfides.

$$(NH_4)_2S + xS = (NH_4)_2S_{(x+1)}.$$

The polysulfide solution formed is subjected to heating, during which the polysulfides decompose

$$(NH_4)_2S_{(x+1)} = 2NH_3 + H_2S + xS.$$

On cooling, the NH_3 and H_2S evolved, mixed with water vapor, from the starting solution

$$2NH_3 + H_2S = (NH_4)_2S.$$

After washing and steaming, the coal, now free of sulfur, is reused for gas purification. The physicochemical principles of the process of hydrogen sulfide removal from gases were developed by Ya. D. Zel'venskiy [9]. He established that the kinetics of this process are of an external-diffusion character and are therefore independent of the individual properties of the adsorbent. On the other hand, activated carbons differ substantially in sulfur capacity, which may be explained by the characteristics of their porous structure. As a result of studies on the selection of activated carbons with optimum sulfur capacity, a special brand, the "C coal", has been proposed which is obtained by steam-gas activation of chemically active and low-ash brown coals in a fluidized bed.

The degree of removal of H_2S from the gas on this coal of relatively high mechanical strength is more than 99% for an average sulfur capacity equal to 112% of the weight of the coal or 370 g per 1 l of coal.

In recent years, the removal of hydrogen sulfide from gases by means of activated carbon has been carried out in a fluidized bed, which permits one to achieve an uninterrupted operation and to considerably improve the technical-economic indices.

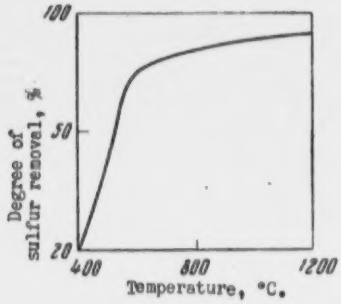


Fig. 5. Temperature dependence of the degree of recovery of hydrogen sulfide from combustible gas by means of calcium oxide.

From the standpoint of the objectives of our study, there is also some interest in the work of Wickert, published at the end of 1963, dealing with the gasification of liquid sulfur-containing fuel with high-temperature removal of hydrogen sulfide from the combustible gas, using calcium oxide dust as the reactant [10]. In this study, the author came to the conclusion that it is possible to achieve a process such that it proves the temperature dependence of the degree of recovery of hydrogen sulfide from a combustible gas with the aid of CaO (Fig. 5).

Wickert suggests that the regeneration of the spent reactant - finely dispersed calcium sulfide - be carried out by treating it in the regenerator with hot water and blowing hot flue gases through it to obtain hydrogen sulfide of high concentration and calcium carbonate in the solid phase.

Wickert emphasizes that under fuel gasification conditions, the presence of CaO will accelerate the reaction between carbon and water vapor, i. e., will decrease the content of soot in the gas in the case of gasification of liquid fuel. The author proposes a process for preparing a sulfur-free gas from the liquid gas whereby hydrogen sulfide is removed from the gas in a fluidized bed of calcium oxide particles at high temperatures (Fig. 6).

Of major interest are also the studies made by V. T. Chagunava [16] on the removal of hydrogen sulfide from coke oven and water gases at room temperature by means of manganese ore (roasted) and also on the removal of organosulfur compounds from synthesis gas and benzene by these reactants at 400-450°C.

On the basis of laboratory experiments carried out in 1957 at one of the nitrogen fertilizer plants, an industrial assembly was built for removing hydrogen sulfide from coke oven gas with manganese peroxide ore, with an output of 15,000 m^3/hr. In 1959, this plant also adopted a manganese method of removal of organosulfur compounds from synthesis gas. The throughput of the assembly at a space velocity of 200 hr^{-1} and a linear velocity of 0.1-0.2 m/sec was 15,000-20,000 m^3/hr.

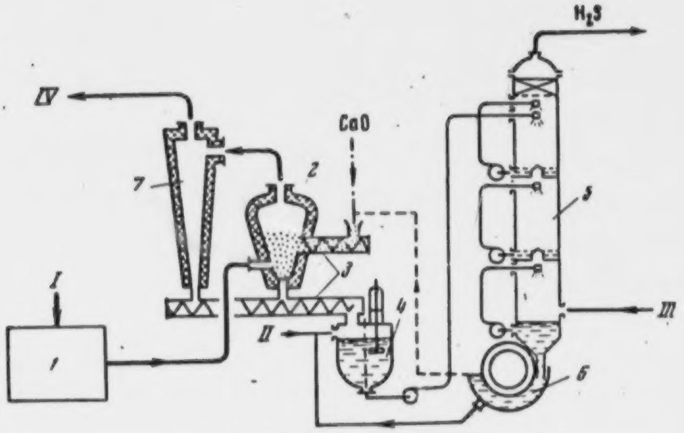


Fig. 6. Flow diagram of the production of sulfur-free gas after Wickert.

1 - gas generator; 2 - reactor; 3 - screw conveyers; 4 - stirer; 5 - column; 6 - drum filter; 7 - cyclone.

Flows: I - fuel; II - water; III - flue gases from boiler; IV - gas to boiler.

The service life of the mass for a sulfur capacity of 3-5%, depending on the content of organosulfur compounds in the gas, ranged from 1 to 3 months. The spent mass was discarded.

The above survey of the processes and methods of hydrogen sulfide removal from gases proposed thus far illustrates rather clearly the extensive development of liquid processes and to a lesser extent, processes of dry sulfur removal from gases.

All these processes are carried out at comparatively low temperatures, and interest in the development of high-temperature processes (above 400°C.) of hydrogen sulfide removal from gases by means of solid reactant, has grown only in the last few years.

The high-temperature process of sulfur removal from gases is as yet insufficiently developed, posing major objectives before researchers.

Selection of Reactants for High-Temperature Removal of Hydrogen Sulfide from Gases and General Characteristics of the Conditions of Regeneration of Solid Residue

The high-temperature removal of hydrogen sulfide from gases is best carried out by means of solid reactants which should be stable at these temperatures, and after reacting with hydrogen sulfide, should yield stable forms of sulfur compounds. From this standpoint, of greatest interest are metals - calcium, magnesium, and barium, whose oxides melt at 2500°C., and whose sulfates and sulfides are stable at temperatures up to 1200°C. Oxides of these metals are present in common inexpensive natural mineral substances such as lime Ca_2CO_3, dolomite $CaMg(CO_3)_2$, and magnesite $MgCO_3$, which can be used as reactants in the high-temperature purification of gases.

Of great importance in this connection will be their dissociation temperature. It should be below the temperature of the principal process of purification of gases by these reactants in order to ensure the conversion of carbonate salts into metal oxides and prevent the formation of such salts when sulfur gases containing carbon dioxide are used. The dissociation temperature of dolomite is 730°C., lime 970°C., and magnesite 640°C. Hence, when lime is used, for example, the process should be carried out at temperatures not below 950°C.

The use of alkaline earth oxides for the removal of hydrogen sulfide from gases at lower temperatures, 600-800°C., is less effective, particularly in the case of gas mixtures containing carbon dioxide. The presence of the latter leads to a wasteful expenditure of reactants on the formation of carbonate salts and requires an additional consumption of heat in the course of regeneration.

Oxides of iron and manganese can be used to remove hydrogen sulfide from gases in the 600-800°C. temperature range. Their use as reactants does not cause the formation of metal acid carbonates. The temperature of dissociation of iron carbonate according to the data of many authors ranges from 360 to 450°C., and for manganese carbonate the start of decomposition takes place at 300°C. As far as the stability of salts of sulfur compounds is concerned, particularly iron and manganese sulfides, their decomposition temperature is above 1200°C. When they are used for the removal of hydrogen sulfide from gases, natural iron and manganese ores can be considered. Thus, iron and manganese oxides may satisfy the requirements for setting up the high-temperature removal of hydrogen sulfide from gases (500-800°C.). Alkaline earth oxides are fundamentally more suitable at higher temperatures.

To set up an economical process of removal of sulfur compounds from gases, it is necessary to consider the characteristics of the solid residue obtained after the reaction. Knowledge of the properties of this residue determines the conditions of regeneration of the solid material and the possibility of a profitable utilization of the recovered sulfur. These characteristics depend on the set of conditions in which the purification process is carried out, and primarily on the composition of the gases. In a reducing gaseous medium, such as is typical of the process of gasification of liquid and solid fuels, chiefly metal sulfides are formed. Their regeneration can be carried out by roasting in a medium of atmospheric air with the formation of metal oxides in the solid residue and sulfur dioxide in the gas.

Regeneration of metal sulfides can also be carried out by use of steam-air treatment and in principle, depending on the steam-to-oxygen ratio in the initial blast, final gas mixtures with different contents of sulfur dioxide and hydrogen sulfide can be obtained. Sulfur dioxide or gas mixtures with it may be used in the production of sulfuric acid or elemental sulfur.

Thus, analysis of the general conditions prevailing in the setting up of processes of high-temperature removal of hydrogen sulfide from gas mixtures shows the expediency of using alkaline earth oxides (CaO, MgO, etc.) and also iron and manganese oxides for this purpose.

The process of regeneration of the solid residue after the reaction may be carried out by roasting or by steam-air treatment of the sulfides obtained.

THERMODYNAMICS OF PROCESSES OF HIGH-TEMPERATURE REMOVAL OF HYDROGEN SULFIDE FROM GASES

The characteristics of the course of low-temperature processes of sulfur removal from gases are insufficient for setting up the processes of gas purification at higher temperatures (500-100°C.), which have their own specific features. The analysis and evaluation of these characteristics requires first of all an examination of the thermodynamic properties of such processes.

Thermodynamics of the Process of Hydrogen Sulfide Removal from Gas Mixtures using Calcium Oxide

The reaction of calcium oxide with hydrogen sulfide is a complex process which in addition to the main reaction

$$CaO + H_2S \rightleftarrows CaS + H_2O - 17.25 \text{ kcal}$$

may involve a reaction of direct thermal decomposition of hydrogen sulfide, and also other reactions between calcium oxide and the products of the main process. When calcium oxide reacts with multicomponent gas mixtures containing hydrogen sulfide, in addition to the indicated reactions there may take place reactions of the individual components with one another and with calcium oxide. In order to determine the thermodynamic characteristics of the entire complex process, it is obviously necessary to have data on the thermodynamics of individually occurring reactions. To this end, calculations were made on the thermodynamic equilibrium of the reaction $CaO + H_2S \rightleftarrows CaS + H_2O$ at 600-1400°C.

The calculations were carried out by using standard values of thermodynamic functions of the individual components of the system (see Appendix).

Values of the equilibrium constant $K_p = p_{H_2O}/p_{H_2S}$ for different temperatures were determined by calculating the values of the free energy of the reaction from the Temkin-Shvartsman equation

$$\Delta Z^{\circ}_T/T = (\Delta H^{\circ}_{298}/T) - \Delta S^{\circ}_{298} - (\Delta a_0 M_0 + \Delta a_1 M_1 + \Delta a_2 M_2 + \Delta a_{-2} \Delta M_{-2}),$$

where ΔH°_{298} and ΔS°_{298} are the heat of formation (cal/mole) and entropy (cal/deg mole) of the components at standard conditions; Δa_0, Δa_1, Δa_2, Δa_{-2} are the coefficients of temperature change of the heat capacity of the system; M_0, M_1, M_2, and M_{-2} are coefficients taken from M. I. Temkin and L. A. Shvartsman's reference table.

The value of K_p was calculated from the equation $\ln K_p = -\Delta Z^{\circ}_T/RT$, where ΔZ is the free energy, cal/mole; R is the universal gas constant, equal to 0.082 l atm/deg, and T is the absolute temperature in °K.

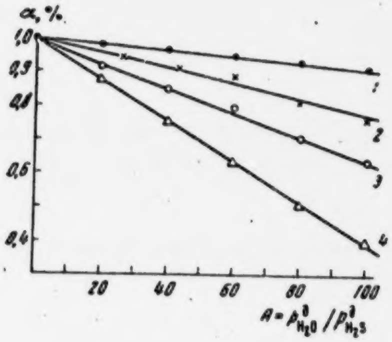


Fig. 7. Equilibrium degree of conversion of hydrogen sulfide vs. content of water vapor in gaseous mixture at different temperatures.

1 - 800°C.; 2 - 900°C.; 3 - 1000°C.; 4 - 1100°C.

The degree of conversion of H_2S at equilibrium is determined from the formula $\alpha = K_p/(1+K_p)$. Results of the calculations, given below, show that in the temperature interval of interest to us, the values of K_p are sufficiently large and α approaches 100%, i. e., the reaction of dry hydrogen sulfide with calcium oxide proceeds almost completely in the direction of formation of water with a practically complete consumption of the hydrogen sulfide supplied:

t, °C	500	700	800	900	1000	1100	1200	1300	1400
$\Delta Z_T/T$	−17,891	−15,769	−13,903	−12,311	−11,190	−10,038	−9,010	−8,081	−7,133
$\ln K_p$	3,91	3,44	3,04	2,69	2,44	2,20	1,97	1,77	1,60
$K_p = p_{H_2O}/p_{H_2S}$	8110	2750	1100	490	275	166	93	59	40
α, %	~100	~100	~100	~100	99,5	99,3	99,0	98,5	97,5

The equilibrium degree of conversion of hydrogen sulfide depends on the content of water vapor in the gaseous mixture.

Figure 7 shows this dependence at various temperatures for different ratios of partial pressures of water vapor and hydrogen sulfide in the initial blast. The degree of conversion α in this case was calculated from the formula

$$\alpha = \frac{K_p - A}{1 + K_p},$$

where $A = p^{\text{н}}_{H_2O}/p^{\text{н}}_{H_2S}$ is the ratio of partial pressures of water vapor and hydrogen sulfide in the blast.

In setting up processes of high temperature removal of hydrogen sulfide from gases, it is necessary to consider the possibility of the reaction of its direct thermal decomposition under certain conditions. For this reason, values of the constants of thermodynamic equilibrium of the reaction $H_2S \rightleftharpoons H_2 + {}^1/_2\, S_2$ were determined at various temperatures [40]:

$$K'_p = p^2_H\, p_S/p_{H_2S}, \quad K''_p = p^2_H/p_{H_2}, \quad K'''_p = p^2_S/p_{S_2},$$
$$K_p = p_{H_2} p^{1/2}_{S_2}/p_{H_2S}, \quad K_p = K'_p/K''_p \cdot \sqrt{K'''_p}.$$

Here account was taken of the fact that in the 700-1400°C. temperature range, which is of interest to us, the sulfur vapor consists mainly of diatomic molecules.

The degree of conversion of hydrogen sulfide during thermal decomposition at equilibrium was calculated from the formula

$$K_p = \frac{\alpha}{1-\alpha}\sqrt{\frac{\alpha p}{2+\alpha}}.$$

The calculated values of the equilibrium constants of the reaction $K_p = p_{H_2} p^{1/2}_{S_2}/p_{H_2S}$ and of the degree of conversion of hydrogen sulfide α at different temperatures are as follows:

t, °C	700	800	900	1000	1100	1200	1300	1400
K_p	$0{,}75\cdot10^{-4}$	$0{,}50\cdot10^{-3}$	$0{,}22\cdot10^{-2}$	$0{,}73\cdot10^{-2}$	0,020	0,044	0,088	0,162
α	0,040	0,048	0,054	0,060	0,095	0,140	0,215	0,320

From the above data it follows that the direct thermal decomposition of hydrogen sulfide is manifested only at temperatures above 1200-1300°C.

Up to 1100°C., the equilibrium degree of conversion during thermal decomposition of hydrogen sulfide does not exceed 10%.

The reaction $H_2S \rightleftarrows H_2 + {}^1/_2 S_2$ is also inhibited when the hydrogen content of the blast is relatively low. For this reason, in the removal of hydrogen sulfide from gaseous mixtures containing hydrogen, the reaction of thermal decomposition of hydrogen sulfide has little effect on the results of the main process. The results of the complex process of hydrogen sulfide removal from gaseous mixtures will be affected to some extent by the reduction of calcium oxide by hydrogen.

In this connection, we calculated the equilibrium constants of the reaction $CaO + H_2 \rightleftarrows Ca + H_2O$ at temperatures from 700 to 1400°C.:

t, °C	700	800	900	1000
$K_p = p_{H_2O}/p_{H_2}$	$1.6 \cdot 10^{-19}$	$1.0 \cdot 10^{-18}$	$5.6 \cdot 10^{-16}$	$1.1 \cdot 10^{-14}$
t, °C	1100	1200	1300	1400
$K_p = p_{H_2O}/p_{H_2}$	$9.5 \cdot 10^{-13}$	$1.6 \cdot 10^{-12}$	$1.3 \cdot 10^{-11}$	$0.8 \cdot 10^{-10}$,

The calculations showed that in the 700-1400°C. range, the effect of the individual reaction of reduction of calcium oxide by hydrogen is slight.

On the basis of the established characteristics of the thermodynamic equilibrium of individually occurring reactions, it was possible to perform a calculation of the equilibrium of the overall process of interaction between the complex hydrogen sulfide-containing gaseous mixture and calcium oxide. As a mixture of this type we took power-producing gas from sulfur mazuts, constituting the mixture $H_2S + H_2O + H_2 + CO + N_2 + CO_2$.

From a thermodynamic standpoint, the determining reactions of these gases with calcium oxide in such a system may be considered to be the following:

$$CaO + H_2S \rightleftarrows CaS + H_2O; \qquad H_2S \rightleftarrows H_2 + {}^1/_2 S_2;$$
$$CaO + H_2 \rightleftarrows Ca + H_2O; \qquad CO + H_2O \rightleftarrows CO_2 + H_2.$$

The equilibrium composition of the gas will be determined by jointly solving a system of equations including equations of equilibrium constants of the individual reactions and the equation of material balance.

The working equations of the process are

$$K'_p = p_{H_2O}/p_{H_2S}; \qquad (1)$$
$$K''_p = p_{H_2}pS_2^{1/2}/p_{H_2}; \qquad (2)$$
$$K'''_p = p_{H_2O}/p_{H_2}; \qquad (3)$$
$$K''''_p = p_{H_2}p_{CO_2}/p_{CO}p_{H_2O}; \qquad (4)$$
$$p^b_{H_2O} + p^b_{H_2S} + p^b_{H_2} = p_{H_2O} + p_{H_2} + p_{H_2S}; \qquad (5)$$
$$P = p_{H_2O} + p_{H_2S} + p_{H_2} + p_{S_2} + p_{N_2} + p_{CO} + p_{CO_2}. \qquad (6)$$

where K_p', K_p'', K_p''', K_p'''' are the equilibrium constants of the respective reactions; p with the corresponding subscripts are the partial pressures of gases at equilibrium; p^b with the corresponding subscripts are the partial pressures of the gases in the initial blast; P is the total pressure.

Using some simple transformations of equations (1) - (3), one can readily determine the value of the partial pressure of sulfur vapor

$$p_{S_2}^{1/2} = K''_p \cdot K'''_p/K'_p.$$

In the 700-1400°C. temperature range, K'' changes from 0.75×10^{-4} to 0.162; K_p''', from 1.6×10^{-19} to 0.8×10^{-10}; K_p', from 2750 to 40.

Consequently, in the indicated temperature range, the partial pressure of sulfur vapor amounts to a negligibly small value.

In determining the most important index of the process of sulfur removal from a gaseous mixture, i. e., the degree of conversion of hydrogen sulfide, we shall write $A = p^b_{H_2O}/p_{H_2S}$ and $B = p^b_{H_2}/p^b_{H_2S}$. Then equation (5) may be written as follows:

$$Ap^b_{H_2S} + p^b_{H_2S} + Bp^b_{H_2S} = K'_p p_{H_2S} + p_{H_2S} + \frac{K'_p}{K'''_p} p_{H_2S},$$

whence

$$\frac{p_{H_2S}}{p^b_{H_2S}} = \frac{1 + A + B}{1 + K'_p + K'_p/K'''_p}.$$

Since the quantity K'_p/K'''_p entering into the denominator of this expression represents a large value, the degree of conversion of hydrogen sulfide in the course of the reaction of sulfur-containing power-producing gas with calcium oxide at 700-1400°C. is practically complete.

Thus, thermodynamic analysis showed the possibility of carrying out the process of removal of hydrogen sulfide from sulfur-containing power-producing gas by calcium oxide at high temperatures.

Considering the thermodynamic evaluation of the conditions of roasting of calcium sulfide for the purpose of regenerating the reactants, we can note that to date this process has not been studied, although a large number of studies on the roasting of sulfides of the metals, chiefly nonferrous ones, have been published in the literature.

In this connection, the authors carried out a thermodynamic analysis of the process of interaction of calcium sulfide with oxygen, the results of which are presented below. The method of calculation was similar to the preceding one.

When calcium sulfide is oxidized, the formation of calcium sulfate or oxide and also free calcium and elemental sulfur is possible, according to the reactions

$$CaS + 2O_2 = CaSO_4; \qquad (7)$$

$$CaS + 1^1/_2O_2 = CaO + SO_2; \qquad (8)$$

$$CaS + O_2 = Ca + SO_2; \qquad (9)$$

$$CaS + {}^1/_2O_2 = CaO + {}^1/_2S_2. \qquad (10)$$

Data on the probability of the reactions in the course of roasting may be obtained by comparing the values of the free energy change of these reactions.

The calculated values of $\Delta Z/T$ for these four reactions are given below:

Temperature, °C. Reaction	600	700	800	900	1000	1100	1200	1300	1400
(7)	—174	—148	—127	—110	—94	—83	—71	—63	—55
(8)	—106	—94	—83	—75	—68	—62	—57	—52	—48
(9)	56	50	46	42	38	36	33	31	29
(10)	23,6	21,1	19,0	17,4	16,2	15,0	14,0	13,1	12,4

Hence, at 600-1400°C., the reaction of calcium sulfide oxidation proceeds toward the formation of $CaSO_4$, CaO, SO_2 и S_2. Reaction (9) at these temperatures is possible only from right to left, so that the formation of metallic calcium according to this reaction is excluded. The probability of oxidation of calcium sulfide according to reaction (7) with formation of $CaSO_4$ is greater than according to reaction (8) with the formation of CaO and SO_2, and considerably exceeds the possibility of formation of elemental sulfur according to reaction (10). At temperatures above 1300°C., the probability of reactions (7) and (8) is practically the same.

Since during roasting of the sulfide in the gaseous mixture oxygen is present together with SO_2, the possibility of oxidation of SO_2 to SO_3 according to the reaction.

$$SO_2 + {}^1/_2O_2 = SO_3. \tag{11}$$

is not excluded.

Values of the free energy $(\Delta Z/T)$ of reaction (11) at different temperatures are given below:

t, °C	600	700	800	900	1000	1100	1200	1300	1400
$-\Delta Z/T$	1,1	3,87	6,24	8,22	9,83	11,25	12,52	13,53	14,45

The free energies of reaction (11) have a positive value, so that at 600-1400°C. the reaction may be neglected.

Numerous studies of the oxidation of metal sulfides established that sulfides in a mixture with sulfates or higher oxides are good reductants for the latter. Considering this point with regard to the oxidation of calcium sulfide, one can propose the following course of the reaction:

$$3CaSO_4 + CaS = 4CaO + 4SO_2. \tag{12}$$

The calculated values of the free energy of reaction (12) are

t, °C	600	700	800	900	1000	1100	1200	1300	1400
$\Delta Z/T$	101,1	72,3	49,0	33,3	14,0	0,8	—10,2	—19,7	—27,9

At 1200°C. and above, calcium sulfate is reduced by calcium sulfide to calcium oxide and sulfur dioxide.

Thus, when calcium sulfide is roasted in the presence of atmospheric oxygen at temperatures above 1200°C. and in the absence of kinetic inhibition, the process may be expected to proceed with the predominant formation of SO_2 and CaO. Under these conditions, the amount of elemental sulfur formed will be minimal. In addition to the temperature effect, this is also due to the fact that the roasting is always carried out with a certain excess of air that promotes the combustion of sulfur to sulfur dioxide.

This can be readily ascertained by analyzing the conditions of simultaneous occurrence of reactions (8) and (10). From the equations for the equilibrium constants of these reactions one can determine the expressions for the partial pressures: $p_{SO_2}=K'_p\,p_{O_2}$, $p_{S_2}=(K''_p)^2\,p_{O_2}$, whence

$$\frac{p_{SO_2}}{p_{S_2}}=\frac{K'_p}{(K''_p)^2}\,p_{O_2}^{1/2}.$$

In the 700-1400°C. temperature range, the value of $K'_p/(K''_p)^2$ is 10^8-10^{12}, and the magnitude of $p_{O_2}^{1/2}$ in the presence of excess oxygen has appreciable values. Therefore, p_{SO_2} is many times greater than p_{S_2}, and the amount of elemental sulfur evolved during the roasting of sulfides will be minimal.

A slightly different composition of the gases may be obtained by treating calcium sulfide with steam and air.

First it should be noted that thermodynamically, favorable conditions are lacking for the regeneration of the sulfide by its direct steam treatment at 500-1300°C. Actually, the process of high-temperature removal of hydrogen sulfide from gases here considered is based on the reaction $CaS + H_2O = CaO + H_2S$, which takes place in the opposite direction.

A more favorable thermodynamic picture is obtained for the steam-air treatment of calcium sulfide (Table 1).

Table 1.

Free Energy Change for Reactions of Calcium Sulfide with a Steam-Air Mixture at Different Temperatures.

Reaction	$\Delta Z/T$ at temperature, °C.					
	500	600	700	800	900	1000
$CaS + H_2O + O_2 = CaO + SO_2 + H_2$	−63,9	−55,9	−49,5	−44,3	−40,1	−36,4
$2CaS + H_2O + 1\frac{1}{2}O_2 = 2CaO + H_2S + SO_2$	−113,1	−98,0	−85,9	−76,1	−68,0	−61,1
$2CaS + H_2O + 1\frac{1}{2}O_2 = 2CaO + SO_2 + \frac{1}{2}S_2 + H_2$	−96,8	−84,9	−75,4	−65,7	−61,3	−55,9
$3CaS + H_2O + 2O_2 = 3CaO + H_2S + SO_2 + \frac{1}{2}S_2$	−145,9	−126,8	−111,7	−99,4	−89,1	−79,8
$2CaS + H_2O + \frac{1}{2}O_2 = 2CaO + H_2S + \frac{1}{2}S_2$	−21,1	−15,7	−11,5	−7,7	−4,6	−2,1

An evaluation of the possible distribution of sulfur between SO_2 and H_2S, based on the formation of elemental sulfur, was made by using the calculated equilibrium constants of the determining reactions:

$$\begin{array}{lll} \text{I.} & CaS + 1^1/_2O_2 = CaO + SO_2, & K'_p = p_{SO_2}/p_{O_2}^{1^1/_2}, \\ \text{II.} & CaS + {}^1/_2O_2 = CaO + {}^1/_2S_2, & K''_p = p_{S_2}^{1/2}/p_{O_2}^{1/2}. \\ \text{III.} & CaS + H_2O = CaO + H_2S, & K'''_p = p_{H_2S}/p_{H_2O}. \end{array}$$

It may be readily established that

$$\frac{p_{SO_2}}{p_{H_2S}} = \frac{K'_p}{K'''_p} \cdot \frac{p_{O_2}^{3/2}}{p_{H_2O}} \quad \text{and} \quad \frac{p_{SO_2}}{p_{S_2}} = \frac{K'_p}{(K''_p)^2} p_{O_2}^{1/2}.$$

In the 600-1000°C. temperature range, the values of K'_p/K''_p change from 1.6×10^{28} to 2×10^{18}, which indicates large values of $(K'_p/K'''_p) \cdot (p_{O_2}^{3/2}/p_{H_2O})$, i. e., a very small content of H_2S in the gas at equilibrium.

The amount of elemental sulfur being liberated is also relatively small, owing to the large values of $K'_p/(K''_p)^2$ in the 600-1000°C. temperature range (10^8-10^{11}) and to the relatively lesser effect of the magnitude of the equilibrium oxygen concentration.

The use of steam-air treatment of sulfides as compared to oxidizing roasting can provide for the regeneration of calcium oxide at temperatures to 1000°C. with the predominant formation of sulfur dioxide, a slightly higher yield of elemental sulfur, and a minimum amount of hydrogen sulfide.

Thermodynamics of the Process of Hydrogen Sulfide Removal from Gaseous Mixtures using Iron Oxides

Thermodynamic studies of the system Fe-S-O-H-C have been conducted mainly by metallurgists in connection with processes of desulfurization of metals. The main purpose of these studies was to elucidate the conditions of transfer of sulfur from solid ferrous sulfide to the gaseous phase and vice versa at high temperatures.

G. Shenk [11] plotted graphically the regions of existence of pure substances consisting of two solid phases Fe_3O_4-FeS, FeO-FeS, and Fe-FeS at temperatures of 627-1327°C. for different compositions of the gaseous phase (O_2, H_2, CO, CO_2, H_2S, SO_2, SO_3, S_2, H_2O). Also known are studies dealing with the thermodynamic equilibrium of a system containing no carbon, Fe-S-O-H [7, 12, 13].

Some studies give thermodynamic calculations for systems consisting of two solid phases, Fe_3O_4-FeS and FeO-FeS, and the equilibrium constants of the reactions are determined without calculating the equilibrium composition of the gas [12, 13].

The most complete study of the equilibrium in the system Fe-S-O-H was made by O. P. Korobeynichev [7], who analyzed the following combinations of two solid phases: Fe_2O_3-Fe_3O_4-FeS_2, Fe_3O_4-FeS-FeS_2, Fe_3O_4-Fe-FeS, Fe_3O_4-FeO-FeS, FeO-Fe-FeS, and calculated the equilibrium gas composition for each of them at temperatures of 300-1200°K.

The published studies, however, do not give a complete picture of the course of the process of interest to us here, i. e., the removal of hydrogen sulfide from combustible carbon-containing gases by means of iron oxides at high temperatures (500-100°C.). For this purpose it is necessary first of all to know the thermodynamic characteristics of the course of the many reactions in the system Fe-S-O-H-C at these temperatures. We therefore calculated values of the free energy for the possible reactions of iron oxides with the hydrogen sulfide present in combustible gases, i. e., in the reducing medium (CO, H_2, CO_2, N_2) at 500-1000°C. The results of these calculations are given in Table 2. As follows from these calculations, if one considers the interaction of iron oxides with hydrogen sulfide in the absence of reducing gases, in the reaction of the lower oxides Fe_2O_3 and Fe_3O_4, their reduction by hydrogen sulfide with the liberation of elemental sulfur in the gaseous phase is observed [reactions (1) and (2)]. The liberation of elemental sulfur in a reducing medium is rather improbable, since it would be hydrogenated, for example, by hydrogen according to reaction (5).

Ferrous oxide and iron with hydrogen sulfide form iron sulfide according to reactions (3) and (4). In a reducing medium, the interaction of iron oxides with hydrogen sulfide can form only iron sulfide in the solid phase, or iron and its lower oxides may be obtained along with the iron sulfide. In the latter case, one solid component is consumed and two other solid phases are formed.

There is a high probability of occurrence of reactions between iron oxides and hydrogen sulfide in a reducing medium with the formation in the solid phase of a single component - iron sulfide [reactions (6)-(9)]. In the overall process of removal of hydrogen sulfide from gases in a reducing medium (H_2,CO), it is evident that in addition to the reactions in which iron oxides combine directly with hydrogen sulfide, the reduction of iron oxides by hydrogen and carbon monoxide to lower oxides will take place. This is confirmed by data on the thermodynamic potential change over the entire range of temperatures from 500 to 1200°C. for reactions (10)-(15). Here the

Table 2.

Change of the Free Energy of the Reactions of Iron Oxides with Hydrogen Sulfide in a Reducing Medium.

Reaction		$\Delta Z/T$ at temperature, °C.							
		500	600	700	800	900	1000	1100	1200
$Fe_2O_3 + 3\,H_2S = 2\,FeS + 3\,H_2O + 0{,}5\,S_2$	(1)	−18,38	−20,26	−21,96	−23,40	−25,06	−26,52	−27,93	−29,32
$Fe_3O_4 + 4\,H_2S = 3\,FeS + 4\,H_2O + 0{,}5\,S_2$	(2)	−23,53	−25,03	−26,51	−27,89	−29,39	−30,80	−32,20	−33,60
$FeO + H_2S = FeS + H_2O$	(3)	−14,67	−13,33	−12,43	−12,10	−11,52	−11,38	−11,40	−11,54
$Fe + H_2S = FeS + H_2$	(4)	−17,18	−15,27	−13,93	−13,41	−12,48	−12,16	−12,03	−12,05
$H_2 + 0{,}5\,S_2 = H_2S$	(5)	−16,73	−13,80	−11,50	−9,66	−8,17	−6,94	−5,93	−5,09
$Fe_2O_3 + 2\,H_2S + H_2 = 2\,FeS + 3H_2O$	(6)	−107,04	−105,81	−105,04	−104,88	−103,56	−104,55	−104,79	−105,19
$Fe_3O_4 + 3\,H_2S + H_2 = 3\,FeS + 4\,H_2O$	(7)	−39,56	−37,92	−36,86	−36,57	−35,91	−35,83	−35,96	−36,24
$Fe_2O_3 + 2\,H_2S + CO = 2\,FeS + 2\,H_2O + CO_2$	(8)	−37,71	−35,16	−33,36	−32,59	−31,33	−30,86	−30,65	−30,66
$Fe_3O_4 + 3\,H_2S + CO = 3\,FeS + 3\,H_2O + CO_2$	(9)	−42,76	−39,83	−37,77	−36,89	−35,41	−34,84	−34,55	−34,49
$2\,Fe_2O_3 + H_2S + H_2 = Fe_3O_4 + FeS + 2\,H_2O$	(10)	−29,91	−29,13	−28,71	−28,72	−28,62	−28,85	−29,24	−29,75
$2\,Fe_3O_4 + H_2S + 2\,H_2 = 5\,FeO + FeS + 3\,H_2O$	(11)	−6,53	−10,08	−12,59	−13,79	−15,47	−16,15	−16,44	−16,42
$2\,FeO + H_2S + H_2 = Fe + FeS + 2\,H_2O$	(12)	−12,65	−11,95	−11,53	−11,46	−11,29	−11,37	−11,57	−11,86
$2\,Fe_2O_3 + H_2S + CO = Fe_3O_4 + FeS + H_2O + CO_2$	(13)	−32,76	−30,59	−29,08	−28,41	−27,40	−27,03	−26,91	−26,98
$Fe_3O_4 + H_2S + CO = 2\,FeO + FeS + H_2O + CO_2$	(14)	−13,11	−12,80	−12,50	−12,25	−11,89	−11,57	−11,23	−10,86
$2\,FeO + H_2S + CO = Fe + FeS + H_2O + CO_2$	(15)	−15,29	−13,20	−11,70	−10,95	−9,88	−9,39	−9,10	−8,97
$9\,Fe_2O_3 + H_2S = 6\,Fe_3O_4 + SO_2 + H_2O$	(16)	−25,24	−31,59	−37,15	−41,43	−46,83	−51,32	−55,65	−59,90
$3\,Fe_3O_4 + 10\,H_2S = 9\,FeS + 10\,H_2O + SO_2$	(17)	−70,24	−73,15	−76,27	−79,57	−82,95	−86,46	−90,15	−93,73
$FeS_2 = FeS + 0{,}5\,S_2$	(18)	−96,48	−89,62	−84,33	−81,19	−76,90	−74,27	−72,16	−70,47

reduction of iron oxides to pure iron according to reactions (12) and (15) is observed.

In principle, reactions of iron oxides with hydrogen sulfide with the formation of iron sulfide and sulfur dioxide in the gaseous phase are also possible [reactions (16) and (17)]. However, in a reducing medium, these reactions may by neglected. O. K. Korobeynichev has estimated the loss of sulfur in the form of SO_2 in the reduction of iron oxides with hydrogen-containing gas to iron, and showed that even at a ratio $(P^o_{H_2} + P^o_{CO})/P_{H_2S}$ equal to 40, this loss does not exceed 0.4%. He also calculated the equilibrium composition of the gaseous phase at different stages of the process for a gaseous mixture of the composition 1% H_2S, 10% H_2, and 89% N_2, at a pressure of 1 atm. Results of the calculations are shown in Table 3.

Table 3.

Equilibrium Composition of Gaseous Phase.

Stage	Gas	Concentration of gas (in %) at temperature (°K)			
		700	800	1000	1200
$Fe_2O_3 \rightleftarrows Fe_3O_4$	SO_2	1	1	1	1
	H_2O	11	11	11	11
	H_2	$\leqslant 1$	$\leqslant 1$	$\leqslant 1$	$\leqslant 1$
	H_2S	$\leqslant 1$	$\leqslant 1$	$\leqslant 1$	$\leqslant 1$
$Fe_3O_4 \rightleftarrows Fe, FeS$	H_2S	10^{-3}	$3{,}3 \cdot 10^{-3}$	No stage	
	H_2	9,5	8,35		
	H_2O	1,5	2,65		
$Fe_3O_4 \rightleftarrows FeO, FeS$	H_2S	No stages		$4 \cdot 10^{-2}$	$1{,}6 \cdot 10^{-1}$
	H_2			5	2,1
	H_2O			5	8,9
$FeO \rightleftarrows FeS$	H_2S			$2{,}9 \cdot 10^{-2}$	$1{,}05 \cdot 10^{-1}$
	H_2			7 ,3	6,6
	H_2O			3 ,7	4,6
$Fe \rightleftarrows FeS$	H_2S	$1{,}1 \cdot 10^{-3}$	$4{,}4 \cdot 10^{-3}$	$4{,}4 \cdot 10^{-2}$	$1{,}7 \cdot 10^{-1}$
	H_2	11	11		

In the process of hydrogen sulfide removal from gases by iron oxides in the solid phase, the formation of only iron sulfide is most probable; as far as a pyrite medium (FeS_2) is concerned, it is unstable in this temperature range, as is confirmed by the negative value of the free energy of reaction (18). Experimental data of a thermographic analysis performed by several authors [14] also showed that this process takes place vigorously at 520-530°C. Thus, thermodynamic analysis of reactions between iron oxides and hydrogen sulfide in a reducing medium showed that hydrogen sulfide can be recovered from combustible gases at 500-1000°C.

Considering the thermodynamic evaluation of the conditions of regeneration of solid absorbents in the removal of H_2S from gases by means of iron oxides, it is necessary to note the large number of publications devoted to the process of oxidation of iron sulfide by atmospheric oxygen. The investigators were chiefly interested in problems connected with the mechanism of oxidation of iron sulfide by oxygen.

The equilibrium reactions in the system Me-S-O were studied by G. Shenk [11], W. Reinders [15], and others. Shenk [11] investigated the equilibrium conditions of the solid phases Fe_2O_3-FeS as a function of the composition of gaseous mixtures containing O_2, SO_2, SO_3, and also gave a graphical representation of the regions of existence of the solid phases Fe_3O_4-FeS, FeO-FeS, and Fe-FeS in the presence in the gaseous phase of the following components: SO_2, SO_3, S_2, O_2, CO, CO_2, H_2, H_2O at 600-1600°C.

Several studies have dealt with the transfer of sulfur from the solid phase FeS to the gaseous phase by means of the solid components Fe_2O_3, Fe_3O_4 and FeO according to the reactions.

$$3\,Fe_3O_4 + FeS \rightleftarrows 10\,FeO + SO_2,$$
$$2\,FeO + FeS \rightleftarrows 3\,Fe + SO_2.$$

The studies showed that under equilibrium conditions, FeS oxidizes to Fe_2O_3 at a temperature as low as 850°C., and the oxidation of Fe_3O_4 occurs only in the range of 1300-1350°C.; if excess FeS is present, metallic iron may also be formed. The process of desulfurization of the metal is possible only at high temperatures.

In order to achieve a rational organization of the process of regeneration of the solid reactant for its subsequent utilization in cycles of hydrogen sulfide absorption from gases, it is necessary to evaluate the equilibrium of the individual reactions that are possible in the overall process of oxidation of iron sulfide by oxygen.

Table 4 gives the results of calculations of free energy values under different conditions for a series of reactions possible during oxidation of iron sulfide by atmospheric oxygen.

As is evident from the data of Table 4, at 500-1200°C., the reactions of iron sulfide oxidation by oxygen (1)-(4) proceed mainly in the direction of formation of iron oxides in the solid phase and sulfur dioxide in the gaseous phase.

Table 4.

Free Energy Change of the Reactions of Iron Sulfide with Oxygen.

Reaction		ΔZ/T at temperature, °C.							
		500	600	700	800	900	1000	1100	1200
$FeS + O_2 = Fe + SO_2$	(1)	—120,69	—106,27	—94,62	—86,87	—76,60	—69,83	—63,69	—58,25
$FeS + 1,5\,O_2 = FeO + SO_2$	(2)	—125,60	—108,50	—94,71	—83,36	—73,80	—65,62	—58,49	—51,24
$3\,FeS + 5\,O_2 = Fe_3O_4 + 3\,SO_2$	(3)	—534,25	—386,79	—336,97	—304,33	—262,23	—233,34	—208,45	—186,76
$2\,FeS + 3,5\,O_2 = Fe_2O_3 + 2\,SO_2$	(4)	—318,04	—275,28	—241,35	—213,86	—191,08	—171,92	—155,58	—132,25
$FeS + 2\,O_2 = FeSO_4$	(5)	—167,00	—136,94	—112,80	—96,95	—76,36	—62,15	—49,83	—36,60
$3\,FeSO_4 + FeS = 4\,FeO + 4\,SO_2$	(6)	—1,96	—24,07	—41,71	—56,07	—68,01	—78,09	—86,70	—107,30
$FeS + 0,5\,O_2 = FeO + 0,5\,S_2$	(7)	—91,46	—80,73	—71,84	—65,88	—58,18	—52,74	—47,96	—43,69
$2\,FeS + 1,5\,O_2 = Fe_2O_3 + S_2$	(8)	—126,63	—108,72	—94,34	—84,93	—72,56	—64,02	—56,59	—50,01
$3\,FeS + 2O_2 = Fe_3O_4 + 1,5\,S_2$	(9)	—165,83	—142,02	—109,99	—93,51	—81,98	—71,91	—63,02	—55,07
$0,5\,S_2 + O_2 = SO_2$	(10)	—54,61	—46,30	—39,69	—35,44	—29,87	—26,12	—22,92	—20,16
$FeS + 2\,O_2 = FeO + SO_3$	(11)	—134,72	—114,28	—97,90	—87,18	—73,12	—63,61	—55,30	—48,02
$3\,FeS + 6,5\,O_2 = Fe_3O_4 + 3\,SO_3$	(12)	—472,85	—400,26	—342,32	—304,75	—255,71	—222,36	—193,73	—168,85
$2\,FeS + 4,5\,O_2 = Fe_2O_3 + 2\,SO_3$	(13)	—545,02	—494,02	—453,28	—426,83	—392,27	—368,72	—348,46	—330,82
$FeO + SO_3 = FeSO_4$	(14)	—31,82	—22,14	—14,33	—9,16	—2,49	+2,15	+6,19	+9,74

Despite the probability of oxidation of iron sulfide by atmospheric oxygen to metallic iron, the latter in the presence of excess oxygen is almost completely oxidized to ferrous oxide (FeO). This is confirmed by data of thermodynamic studies carried out by G. Shenk [11].

The formation of iron sulfate in the solid phase according to reaction (5) is probable at 500-1200°C., and its reduction by iron sulfide to ferrous oxide is possible according to reaction (6). Numerous investigations of the oxidation of metal sulfides by oxygen have confirmed the fact of lowering of the decomposition temperature of sulfates in the presence of reductants, i. e., metal sulfides.

There exist favorable thermodynamic conditions of liberation of elemental sulfur according to reactions (7)-(9), but in the presence of excess oxygen sulfur will be oxidized by the latter to sulfur dioxide according to reaction (10). In principle, the formation of sulfur trioxide is also possible in accordance with reactions (11)-(13) during oxidation of iron sulfide by oxygen. However, the theory of metallurgical processes notes that sulfur trioxide is an unstable compound at high temperatures. This is indicated by positive values of the free energies of the reaction $SO_2 + \frac{1}{2}O_2 = SO_3$ at 600-1400°C.

It is difficult to postulate the possibility of formation of iron sulfate in the course of roasting at temperatures above 900°C., as is evident from the results of calculation of the free energy from reaction (14). It has been experimentally established that the temperature of the start of thermal decomposition of iron sulfate is 450-550°C.

Iron sulfate formed by an amorphous oxide is a relatively unstable compound at temperatures above 500°C., which is important for the roasting process.

Thus, thermodynamic analysis of the reactions of oxidation of iron sulfide by oxygen shows that in the course of roasting, iron oxides are primarily formed in the solid phase and sulfur dioxide in the gaseous phase.

If we now consider the thermodynamic evaluation of the conditions of steam-air treatment of iron sulfide, we can note first of all that, in the case of calcium sulfide, direct treatment with water vapor has little effect. This is illustrated by Table 5, which gives values of the free energies of different reactions of iron sulfide with water vapor at 500-1200°C.

The necessary regeneration of solid reactants is thermodynamically possible only in the steam-air treatment of iron sulfide, as is demonstrated by the results, given in Table 6, of calculations of the free energies of different reactions between iron sulfide and a steam-air blast of different compositions at 300-1000°C. Here the formation of metallic iron is rather improbable, and the process is directed toward the formation of its oxides.

Table 5.

Free Energy Change of the Reactions of Iron Sulfide with Water Vapor at Different Temperatures.

Reaction	$\Delta Z/T$ at temperature, °C.							
	500	600	700	800	900	1000	1100	1200
$FeS + H_2O = FeO + H_2S$	+14,7	+13,3	+12,4	+12,1	+11,5	+11,4	+11,4	+11,5
$FeS + 3H_2O = FeO + SO_2 + 3H_2$	+63,3	+54,2	+47,1	+41,5	+36,9	+33,1	+30,1	+27,5
$2FeS + 3H_2O = Fe_2O_3 + 3H_2 + S_2$	+66,7	+59,2	+53,4	+48,9	+45,3	+42,5	+40,2	+38,5
$2FeS + 7H_2O = Fe_2O_3 + 7H_2 + 2SO_2$	+131,6	+114,8	+101,6	+90,9	+82,3	+75,1	+69,1	+64,1
$3FeS + 4H_2O = Fe_3O_4 + 4H_2 + 1,5S_2$	+99,6	+87,3	+78,0	+70,6	+64,8	+60,2	+56,6	+53,7
$3FeS + 10H_2O = Fe_3O_4 + 10H_2 + 3SO_2$	+185,1	+158,1	+140,4	+127,8	+111,4	+100,5	+91,4	+83,6

An evaluation of the thermodynamically probable distribution of sulfur between SO_2, H_2S and elemental sulfur in the course of steam-air regeneration of the sulfide may be approximated by analyzing a system consisting of the three determining equations of the process which include all the reacting components:

$$2FeS + 2O_2 + H_2O = Fe_2O_3 + H_2S + SO_2,$$

$$K_p' = p_{SO_2} \cdot p_{H_2S} / p_{H_2O} \cdot p_{O_2}^2,$$

$$3FeS + O_2 + H_2O = 3FeO + H_2S + S_2,$$

$$K_p'' = p_{H_2S} \cdot p_{S_2} / p_{O_2} \cdot p_{H_2O},$$

$$3FeS + 2O_2 + 2H_2O = Fe_3O_4 + 2H_2S + SO_2,$$

$$K_p''' = p_{H_2S}^2 \cdot p_{SO_2} / p_{O_2}^2 \cdot p_{H_2O}^2.$$

Using some simple transformations, one can readily show that

$$\frac{p_{SO_2}}{p_{H_2S}} = \frac{(K_p')^2}{K_p'''} \cdot \frac{(p_{O_2})^2}{p_{H_2O}},$$

$$\frac{p_{SO_2}}{p_{S_2}} = \frac{K_p'}{K_p''} \cdot \frac{p_{O_2}}{p_{H_2O}}.$$

Table 6.

Free Energy Change of Reactions of Iron Sulfide with a Steam-Air Mixture.

Reaction	$\Delta Z/T$ at temperature, °C.							
	300	400	500	600	700	800	900	1000
$FeS + 1/2\,O_2 + H_2O = Fe + SO_2 + H_2$	+6,0	+3,8	+2,4	+1,4	+0,7	+0,4	+0,3	+0,3
$FeS + O_2 + H_2O = FeO + SO_2 + H_2$	+89,7	+77,5	+68,5	+61,7	+56,5	+52,4	+49,1	+46,5
$2\,FeS + 1/2\,O_2 + H_2O = 2\,FeO + S_2 + H_2$	+0,8	−0,6	−1,4	−1,7	−1,7	−1,3	−0,8	−0,1
$2\,FeS + 1/2\,O_2 + H_2O = 2\,Fe + H_2S + O_2$	+30,2	+23,4	+19,7	+16,8	+14,9	+13,4	+13,0	+12,6
$2\,FeS + 1/2\,O_2 + H_2O = 2\,Fe + SO_2 + 1/2\,S_2 + H_2$	+55,6	+43,9	+35,6	+29,6	+25,1	+21,8	+19,3	+17,6
$2\,FeS + O_2 + H_2O = Fe_2O_3 + S_2 + H_2$	−88,6	−72,1	−59,6	−49,7	−41,7	−34,3	−29,1	−24,1
$2\,FeS + 1^1/_2\,O_2 + H_2O = 2\,FeO + H_2S + SO_2$	−160,5	−133,4	−114,0	−98,3	−85,4	−74,7	−65,5	−57,4
$2\,FeS + 2\,O_2 + H_2O = Fe_2O_3 + H_2S + SO_2$	−248,2	−203,7	−170,4	−144,6	−123,8	−106,7	−92,2	−79,9
$2\,FeS + 2\,O_2 + H_2O = Fe_2O_3 + SO_2 + 1/2\,S_2 + H_2$	−222,3	−183,3	−154,2	−131,5	−113,3	−98,2	−85,5	−74,0
$2\,FeS + 3\,O_2 + H_2O = Fe_2O_3 + 2\,SO_2 + H_2$	−346,1	−284,6	−238,8	−203,3	−174,8	−151,5	−131,9	−115,2
$3\,FeS + O_2 + H_2O = 3\,FeO + H_2S + S_2$	−73,9	−65,7	−60,1	−56,0	−53,1	−50,8	−49,1	−47,8
$3\,FeS + 2\,O_2 + 2\,H_2O = Fe_3O_4 + 2\,H_2S + SO_2$	−241,7	−198,1	−165,4	−139,9	−119,4	−102,5	−88,3	−76,0
$3\,FeS + 2\,O_2 + H_2O = 3\,FeO + SO_2 + S_2 + H_2$	−177,1	−149,2	−128,0	−111,2	−97,3	−85,6	−75,5	−66,5
$3\,FeS + 2^1/_2\,O_2 + H_2O = Fe_3O_4 + SO_2 + S_2 + H_2$	−284,9	−240,0	−207,3	−182,7	−163,7	−148,7	−137,7	−126,9
$3\,FeS + 4^1/_2\,O_2 + H_2O = Fe_3O_4 + 3\,SO_2 + H_2$	−547,5	−454,7	−385,6	−332,0	−288,9	−254,2	−224,8	−199,9
$4\,FeS + 1^1/_2\,O_2 + 3\,H_2O = 2\,Fe_2O_3 + 3\,H_2S + 1/2\,S_2$	−144,8	−110,6	−85,6	−64,2	−47,4	−33,4	−21,3	−10,8
$4\,FeS + 2^1/_2\,O_2 + H_2O = 4\,FeO + H_2S + SO_2 + S_2$	−248,9	−209,3	−179,1	−155,3	−135,7	−119,8	−104,9	−92,2
$4\,FeS + 3^1/_2\,O_2 + H_2O = 2\,Fe_2O_3 + H_2S + SO_2 + S_2$	−480,8	−396,6	−333,5	−288,4	−245,0	−212,4	−185,0	−161,4
$4\,FeS + 4^1/_2\,O_2 + H_2O = 4\,Fe + H_2S + SO_2 + S_2$	+129,7	+104,5	+86,6	+73,6	+63,9	+56,1	+51,4	+47,5
$6\,FeS + 2\,O_2 + 4\,H_2O = 2\,Fe_3O_4 + 4\,H_2S + S_2$	−251,9	−173,6	−141,6	−116,4	−95,8	−78,5	−63,8	−50,9
$6\,FeS + 3^1/_2\,O_2 + H_2O = 2\,Fe_3O_4 + 3\,S_2 + H_2$	−382,4	−316,4	−266,9	−228,1	−196,8	−170,5	−148,8	−129,8
$6\,FeS + 4^1/_2\,O_2 + H_2O = 2\,Fe_3O_4 + H_2S + SO_2 + 2\,S_2$	−594,6	−491,9	−415,0	−355,0	−306,6	−267,1	−233,1	−204,2

As was shown by the calculations, the values of K'_p in the 300-100°C. temperature range changed from 10^{54} to 10^{18}, and the values of K''_p and K'''_p from 10^{16} and 10^{52} to 10^{10} and 10^{17} respectively. For this reason the ratios p_{SO_2}/p_{H_2S} and p_{SO_2}/p_{S_2} will be very large, i. e., hydrogen sulfide and elemental sulfur will be obtained in minimum amounts.

Thus, the steam-air treatment of iron sulfide as compared with oxidizing roasting can be carried out at lower temperatures, but the gas obtained will contain chiefly sulfur dioxide.

Thermodynamics of the Process of Hydrogen Sulfide Removal from Gaseous Mixtures Using Manganese Oxides

As was indicated earlier, in principle, manganese oxides are suited for the removal of hydrogen sulfide from gases at high temperatures. It is evident that the practical realization of such a process will make it necessary to utilize natural manganese ores.

The majority of natural manganese compounds consist of complex oxides of manganese with a valence ranging from two to seven. The most common natural oxide is manganese dioxide, which is found in the form of the mineral pyrolusite. Natural manganite, which contains manganese dioxide and manganous oxide, is also widely distributed.

Since gaseous mixtures from which hydrogen sulfide is removed contain active reducing components for metal oxides, the process of purification may include a varied set of simultaneous reactions - not only the reaction of hydrogen sulfide with manganese oxides, but also the reduction of these oxides. Here one may also observe reactions of hydrogen sulfide with higher and lower manganese oxides resulting in a stable sulfide form of manganese, and also the reduction of higher manganese oxides to lower ones and to the pure metal. In addition to these reactions, the possibility of liberation of elemental sulfur and formation of sulfur dioxide in the gaseous phase is not excluded.

Analysis of literature data on this question has shown that no detailed thermodynamic studies have been made to date on the entire problem of interaction of various manganese oxides with hydrogen sulfide in a reducing medium, if one does not consider studies of the thermodynamics of the reaction between manganous oxide and hydrogen sulfide. Ref. [16] discussed the thermodynamics of this reaction at 400-1000°C. for the process of desulfurization of benzene with a contact mass consisting of manganous oxide. It was noted that such a reaction is possible in this temperature interval.

In order to evaluate the course of the entire process as a whole when manganese oxides are used for the removal of hydrogen sulfide from a combustible gas in a reducing medium, it is necessary to determine the probability of numerous reactions of these oxides with hydrogen sulfide, resulting in the formation of manganese sulfide. Since the composition of the initial ore contains mainly manganese dioxide, the initial interaction will obviously take place in the direction of a reaction of manganese dioxide with hydrogen sulfide, resulting in the formation of manganese sulfide, and in the simultaneous reduction of manganese dioxide by hydrogen and carbon monoxide to lower manganese oxides.

Subsequently, the lower manganese oxides either will react with hydrogen sulfide also to form manganese sulfide along with manganous oxide and manganese, or reactions involving only the formation of manganese sulfide will take place.

In order to obtain a quantitative evaluation of the thermodynamic probability of the occurrence of reactions between manganese oxides and hydrogen sulfides in a reducing medium, a comparison of their free energies was made.

Table 7 gives the results of a calculation of the free energies for numerous reactions of hydrogen sulfide with manganese oxides at 500-1200°C. On this basis, one can determine the highest probability of reactions of manganese dioxide with hydrogen sulfide in a medium of hydrogen and carbon monoxide [reactions (1)-(4) and (13)-(15)], resulting in the formation of manganese sulfide and lower manganese oxides at 500-1000°C.

Other reactions taking place at these temperatures are (5), (6), (16) and (17), which represent the interaction of manganese oxide and manganomanganic oxide with hydrogen sulfide and result in the formation of lower oxides of manganes and its sulfide. The occurrence of reactions of manganous oxide with hydrogen sulfide in a reducing medium, resulting in the formation of manganese sulfide and pure manganese, is improbable.

The absence of metallic manganese in these reactions is confirmed by the experimental studies of V. T. Chagunava dealing with the interaction of hydrogen sulfide with manganese oxides at 300-400°C. Chagunava explains this by the fact that manganous oxide and manganese sulfide have the same crystal structure, and therefore the reactions of manganese oxides with hydrogen sulfide involve sulfidization of manganous oxide without its reduction to the pure metal. On the contrary, when iron oxides are used for the removal of hydrogen sulfide from a gas, as was noted earlier, the sulfidization of iron is associated with the process of its reduction to the pure form.

Furthermore, as is evident from Table 7, there is a high probability of reactions between manganese oxides and hydrogen sulfide in the presence of hydrogen and carbon monoxide only up to the formation of manganese sulfide [reactions (8)-(12) and (19)-(21)].

Considering that manganese disulfide may be present in the solid phase along with manganese sulfide, we calculated the free energies of the reaction of thermal decomposition of manganese disulfide at the indicated temperatures. The calculations, whose results are presented in Table 7, revealed a positive value of this quantity only at 500°C., indicating the thermal stability of manganese disulfide [reaction (31)]. Starting at 600°C. and higher, the free energy values are negative, i. e., thermal decomposition occurs. Consequently, at temperatures above 600°C., the formation of manganese disulfide is excluded. It was important also to evaluate the probability of liberation of elemental sulfur in the course of removal of hydrogen sulfide from the gas.

The overall process of interaction of manganese dioxide with hydrogen sulfide up to the formation of lower oxides of manganese, manganese sulfide and elemental sulfur is described by reactions (22)-(25).

From the data listed in Table 7 it is evident that the probability of the indicated reactions is high.

However, it should be pointed out that in the reaction of hydrogen sulfide with manganese oxides at room temperature, V. T. Chagunava observed the liberation of elemental sulfur only in a neutral medium, whereas in a reducing medium this liberation was absent. For this reason, the degree of recovery of manganese in the neutral medium was lower (93-94%) than in the reducing medium (97-98%).

As is evident from Table 7, in the indicated temperature range there are favorable conditions for the occurrence of reaction (29), i. e., hydrogenation of sulfur by hydrogen with the formation of hydrogen sulfide.

The formation of sulfur dioxide is possible according to reactions (26)-(28). On the basis of calculation of the free energy values it may be assumed that no suitable conditions exist for the occurrence of these reactions at 500-1200°C.

It was important to evaluate reaction (30) of thermal decomposition of manganese carbonate. It is evident from Table 7 that there is a probability that this reaction will take place at 500-1200°C., i. e., at these temperatures manganous oxide will not react with carbon dioxide.

When hydrogen sulfide is removed from the gas by manganese oxides at 600-800°C., manganese carbonate will not be formed.

Thus, the performed thermodynamic analysis of numerous reactions of manganese oxides with hydrogen sulfide in a reducing medium showed that the

Table 7.

Free Energy Change of Reactions between Mangarese Oxides and Hydrogen Sulfide in a Reducing Medium.

Reaction		$\Delta Z/T$ at temperature, °C.							
		500	600	700	800	900	1000	1100	1200
$3\ MnO_2 + H_2S + 2\ H_2 = Mn_2O_3 + MnS + 3\ H_2O$	(1)	−128,20	−116,66	−107,43	−99,91	−93,67	−88,41	−83,92	−80,05
$4\ MnO_2 + H_2S + 3\ H_2 = Mn_3O_4 + MnS + 4\ H_2O$	(2)	−180,36	−163,86	−157,04	−139,79	−130,79	−123,18	−116,66	−111,03
$2\ MnO_2 + H_2S + 2\ H_2 = MnO + MnS + 3\ H_2O$	(3)	−109,21	−100,06	−92,72	−86,49	−81,76	−77,55	−73,95	−70,84
$2\ MnO_2 + H_2S + 3H_2 = Mn + MnS + 4\ H_2O$	(4)	−71,15	−66,80	−64,48	−60,93	−57,98	−55,89	−54,13	−52,60
$2\ Mn_2O_3 + H_2 + H_2S = Mn_3O_4 + MnS + 2\ H_2O$	(5)	−45,01	−42,65	−39,47	−36,88	−34,73	−32,90	−31,35	−30,0
$2\ Mn_3O_4 + H_2S + 2\ H_2 = 5\ MnO + MnS + 3\ H_2O$	(6)	−61,16	−58,74	−56,77	−55,13	−53,74	−52,54	−51,48	−49,38
$2\ MnO + H_2S + 2\ H_2 = Mn + MnS + 2\ H_2O$	(7)	+57,22	+54,15	+51,78	+49,90	+48,38	+47,12	+46,06	+45,16
$MnO_2 + H_2S + H_2 = MnS + 2\ H_2O$	(8)	−59,83	−54,32	−49,92	−44,36	−41,96	−37,98	−36,67	−32,99
$Mn_2O_3 + 2\ H_2S + H_2 = 2\ MnS + 3\ H_2O$	(9)	−54,76	−50,36	−46,88	−44,07	−43,86	−39,38	−38,21	−36,83
$Mn_3O_4 + 3\ H_2S + H_2 = 3\ MnS + 4\ H_2O$	(10)	−130,99	−118,54	−108,66	−100,68	−94,12	−88,64	−84,0	−80,06
$MnO + H_2S = MnS + H_2O$	(11)	−14,05	−12,77	−11,77	−10,98	−10,35	−9,83	−9,41	−9,06
$Mn + H_2S = MnS + H_2$	(12)	−52,48	−46,42	−41,67	−37,86	−34,74	−32,14	−29,96	−28,09
$3\ MnO_2 + H_2S + 2\ CO = Mn_2O_3 + MnS + + 2\ CO_2 + H_2O$	(13)	−135,03	−120,94	−109,75	−100,34	−93,20	−86,92	−81,65	−77,0
$2\ MnO_2 + H_2S + 2\ CO = MnO + MnS + + 2\ CO_2 + H_2O$	(14)	−115,51	−103,78	−94,43	− 88,46	−80,58	−75,32	−70,83	−66,98
$2\ MnO_2 + H_2S + 3\ CO = Mn + MnS + + 3\ CO_2 + H_2O$	(15)	−81,50	−73,39	−66,98	−62,92	−57,53	−53,95	−50,95	−48,37
$2\ Mn_2O_3 + H_2S + CO = Mn_3O_4 + MnS + + CO_2 + H_2O$	(16)	−49,29	−43,83	−39,48	−36,46	−32,97	−30,46	−28,29	−26,39
$Mn_3O_4 + H_2S + CO = 2\ MnO + MnS + + CO_2 + H_2O$	(17)	−41,20	−38,12	−35,69	−34,19	−32,14	−30,81	−29,68	−28,72

Table 7 (continued)

Reaction	$\Delta Z/T$ at temperature, °C.							
	500	600	700	800	900	1000	1100	1200
$2\,MnO + H_2S + CO = Mn + MnS + H_2O + CO_2$ (18)	+20,55	+18,23	+16,35	+15,06	+13,43	+12,25	+11,21	+10,28
$MnO_2 + H_2S + CO = MnS + H_2O + CO_2$ (19)	−113,36	−107,72	−100,56	−95,81	−91,75	−88,25	−85,16	−82,0
$Mn_2O_3 + 2\,H_2S + CO = 2\,MnS + 2\,H_2O + CO_2$ (20)	−30,14	−24,42	−19,86	−16,15	−13,05	−10,41	−8,15	−6,19
$Mn_3O_4 + 3\,H_2S + CO = 3\,MnS + 3\,H_2O + CO_2$ (21)	−68,98	−63,25	−58,76	−55,19	−52,24	−49,81	−44,76	−46,01
$3\,MnO_2 + 3\,H_2S = Mn_2O_3 + MnS + 3\,H_2O + S_2$ (22)	−94,96	−89,34	−84,81	−81,76	−77,89	−75,19	−72,84	−70,78
$5\,MnO_2 + 6\,H_2S = Mn_3O_4 + 2\,MnS + 6\,H_2O + 2\,S_2$ (23)	−176,73	−165,88	−157,89	−152,53	−145,65	−140,83	−136,61	−132,89
$2\,MnO_2 + 3\,H_2S = MnO + MnS + 3\,H_2O + S_2$ (24)	−75,98	−72,76	−70,12	−68,31	−66,01	−64,36	−62,90	−61,59
$MnO_2 + 2\,H_2S = MnS + 2\,H_2O + S_2$ (25)	−12,89	−17,46	−21,05	−23,31	−26,29	−28,25	−29,89	−31,28
$9\,Mn_2O_3 + H_2S = 6\,Mn_3O_4 + SO_2 + H_2O$ (26)	+116,78	+120,63	+123,84	+126,10	+128,97	+131,11	+133,03	+134,80
$3\,Mn_3O_4 + 10\,H_2S = 9\,MnS + 10\,H_2O + SO_2$ (27)	+364,54	+311,37	+268,89	+241,24	+205,40	+181,00	+160,10	+142,00
$2\,MnO + H_2S = 2\,Mn + SO_2 + H_2$ (28)	+110,51	+93,08	+79,22	+70,32	+58,62	+50,74	+44,71	+38,18
$0{,}5\,S_2 + H_2 = H_2S$ (29)	−16,73	−13,80	−11,50	−9,66	−8,17	−6,94	−5,93	−5,09
$MnCO_3 = MnO + CO_2$ (30)	−3,59	−6,03	−7,55	−8,39	−8,72	−8,65	−8,27	−7,64
$MnS_2 = MnS + 0{,}5\,S_2$ (31)	+1,32	−1,17	−3,16	−4,803	−6,18	−7,37	−8,28	−9,27

removal of hydrogen sulfide from the gas may be carried out with manganese oxides at 500-1000°C. with the formation of manganese sulfide in the solid phase.

In evaluating the conditions of regeneration of manganese sulfide by its oxidation with oxygen, it should be noted that almost no studies have been made of this problem. Obviously, this is explained by the absence of large deposits of manganese sulfide and its limited industrial uses. Only thermodynamic calculations of the values of the free energy of formation and dissociation pressure of manganese sulfide at various temperatures have been published [17, 19].

Metallurgists have been chiefly interested in problems of desulfuration of slags in steelmaking. As was noted in [11], the process of desulfuration involves, among other reactions, the reaction Mn + FeS = MnS + Fe. G Shenk [11] discussed the equilibrium conditions of this reaction in the metallurgical process. A study of the kinetics and mechanism of the reaction of manganese sulfide with oxygen at 25-400°C. is discussed in Ref. [18]. A compound of the composition MnS_2O_8 was observed in the solid phase in this temperature range. Decomposition of this compound begins at 500°C. No studies have been made on the oxidation of manganese sulfide at temperatures above 500°C.

Table 8 shows the free energies values for some reactions occurring during the oxidation of manganese sulfide by atmospheric oxygen. Gas is evident from this table, there is a distinct possibility of reactions between manganese sulfide and oxygen up to the formation of manganese and lower oxides in the solid phase, and also sulfur dioxide in the gaseous phase at temperatures from 500 to 1200°C. [reactions (1)-(5)].

In the solid phase, in the oxidation of manganese sulfide by oxygen, the formation of manganese sulfate is also possible according to reaction (6). Manganese sulfate in turn may react with manganese sulfide according to reaction (7) with the evolution of sulfur dioxide and manganese oxide at 500-1200°C. The probability of the occurrence of this reaction increases with rising temperature. When manganese sulfide is oxidized by atmospheric oxygen in the gaseous phase, the evolution of sulfur trioxide may be observed in the gaseous phase, and of manganese oxides in the solid phase according to reactions (8)-(10) at the above-indicated temperatures. However, sulfur trioxide reacting with manganous oxide according to reaction (11) will form manganese sulfate. In addition, as we have noted, sulfur trioxide will be less stable with rising temperature.

The evolution of sulfur is possible according to reactions (12)-(14), whose occurrence is due to the negative values of the free energy at 500-1200°C. Sulfur in turn may burn to sulfur dioxide [reaction (15)] at 500-1200°C.

Table 8.

Free Energy Change of Reactions of Manganese Sulfide with Oxygen.

Reaction		$\Delta Z/T$ at temperature, °C.							
		500	600	700	800	900	1000	1100	1200
$MnS + O_2 = Mn + SO_2$	(1)	−26,03	−22,41	−19,47	−17,48	−14,97	−13,19	−11,64	−10,27
$2\,MnS + 3\,O_2 = 2\,MnO + 2\,SO_2$	(2)	−254,64	−220,42	−192,91	−188,90	−151,83	−135,99	−122,42	−110,58
$MnS + 2\,O_2 = MnO_2 + SO_2$	(3)	−146,48	−123,00	−104,20	−88,29	−75,08	−63,77	−53,96	−45,37
$3\,MnS + 5O_2 = Mn_3O_4 + 3SO_2$	(4)	−172,65	−141,57	−116,67	−96,32	−75,52	−64,85	−52,39	−41,56
$2\,MnS + 3{,}5\,O_2 = Mn_2O_3 + 2\,SO_2$	(5)	−290,53	−249,03	−215,84	−188,35	−165,87	−146,88	−130,59	−116,46
$MnS + 2\,O_2 = MnSO_4$	(6)	−174,96	−144,16	−120,47	−100,88	−84,63	−70,94	−59,26	−49,17
$MnS + 3\,MnSO_4 = 4\,MnO + 4\,SO_2$	(7)	−73,34	−95,12	−113,02	−126,91	−138,22	−147,53	−155,24	−161,78
$MnS + 2O_2 = MnO + SO_3$	(8)	−135,51	−114,97	−99,07	−85,21	−74,09	−64,72	−56,71	−49,73
$3\,MnS + 6{,}5\,O_2 = Mn_3O_4 + 3\,SO_3$	(9)	−450,63	−381,33	−326,17	−290,96	−244,07	−212,98	−185,81	−162,58
$2\,MnS + 4{,}5\,O_2 = Mn_2O_3 + 2\,SO_3$	(10)	−506,26	−458,05	−419,56	−388,29	−362,31	−340,40	−321,67	−305,49
$MnO + SO_3 = MnSO_4$	(11)	−40,35	−29,93	−22,20	−17,33	−10,84	−6,55	−2,90	−0,22
$MnS + 0{,}5\,O_2 = MnO + 0{,}5\,S_2$	(12)	−32,47	−27,98	−24,33	−21,84	−18,76	−16,48	−14,52	−12,79
$2\,MnS + 1{,}5\,O_2 = Mn_2O_3 + S_2$	(13)	−100,33	−84,19	−71,21	−62,62	−51,59	−43,94	−37,31	−31,51
$3\,MnS + 2\,O_2 = Mn_3O_4 + 1{,}5\,S_2$	(14)	−137,05	−115,28	−97,73	−86,05	−71,10	−60,69	−51,64	−43,69
$0{,}5\,S_2 + O_2 = SO_2$	(15)	−54,61	−46,30	−39,69	−35,44	−29,87	−26,12	−22,92	−20,16

Table 9.

Free Energy Change of Reactions of Manganese Sulfide with Water Vapor at Different Temperatures.

Reaction	$\Delta Z/T$ at temperature, °C.							
	500	600	700	800	900	1000	1100	1200
$MnS + H_2O = MnO + H_2S$	+14,1	+12,8	+11,8	+11,0	+10,3	+9,8	+9,4	+9,1
$MnS + 2H_2O = MnO_2 + H_2S + H_2$	+59,9	+54,3	+49,9	+44,4	+42,0	+38,0	+36,7	+33,0
$2MnS + 3H_2O = Mn_2O_3 + 2H_2S + H_2$	+54,8	+50,4	+46,9	+44,1	+43,9	+39,4	+38,2	+36,8
$3MnS + 4H_2O = Mn_3O_4 + 3H_2S + H_2$	+131,0	+118,5	+108,7	+100,7	+94,1	+88,6	+84,0	+80,1

On the basis of a thermodynamic analysis of the numerous reactions occurring in the course of oxidation of manganese sulfide by atmospheric oxygen, the possibility of formation of manganese oxide in the solid phase and of sulfur dioxide in the gaseous phase has been established.

The steam-air treatment of manganese sulfide is characterized by the same thermodynamic properties that were revealed for processes of steam-air treatment of calcium and iron sulfide. Direct treatment of manganese sulfide with water vapor is also ineffective, as indicated by the positive values of the free energies of the corresponding reactions at 500-1200°C., listed in Table 9.

Thermodynamically, only the steam-air treatment is possible, which includes a whole group of different reactions of the steam-air blast with manganese sulfide. Values of the free energies of these reactions at different temperatures are listed in Table 10.

Thermodynamic analysis shows that, as in the case of the steam-air treatment of calcium and iron sulfides, when the steam-air blast reacts with manganese sulfide, the gas obtained will chiefly contain sulfur dioxide and a minimum amount of hydrogen sulfide and elemental sulfur. The solid residue will contain chiefly manganese oxides. The formation of metallic manganese is rather improbable.

EVALUATION OF THE ACTIVITY OF VARIOUS SOLID REACTANTS IN THE PROCESS OF HYDROGEN SULFIDE REMOVAL FROM GASES AT HIGH TEMPERATURES

Thermodynamic studies have shown that the high-temperature removal of

Table 10.

Free Energy Change of Reactions of Manganese Sulfide with a Steam-Air Mixture.

Reaction	ΔZ/T at temperature, °C.							
	300	400	500	600	700	800	900	1000
$MnS + {}^1/_2 O_2 + H_2O = Mn + SO_2 + H_2$	+52,8	+43,5	+36,6	+31,2	+26,9	+23.4	+20,5	+18,0
$MnS + O_2 + H_2O = MnO + SO_2 + H_2$	−90,1	−75,6	−64,9	−56,7	−50,2	−45,0	−40,6	−37,0
$MnS + 1{}^1/_2 O_2 + H_2O = MnO_2 + SO_2 + H_2$	−120,7	−97,8	−80,9	−68,0	−57,7	−49,4	−42,6	−36,8
$2 MnS + {}^1/_2 O_2 + H_2O = 2 Mn + SO_2 + H_2 + {}^1/_2 S_2$	+163,2	+137,3	+118,0	+103,2	+91,3	+81,7	+73,7	+66,9
$2 MnS + {}^1/_2 O_2 + H_2O = 2 Mn + SO_2 + H_2S$	+123,7	+103,2	+88,0	+76,4	+67,1	+59,6	+53,3	+48,0
$2 MnS + O_2 + H_2O = Mn_2O_3 + S_2 + H_2$	−63,7	−47,8	−36,1	−27,1	−20,1	−14,4	−9,7	−5,8
$2 MnS + 1{}^1/_2 O_2 + H_2O = 2 MnO_2 + S_2 + H_2$	−59,7	−48,1	−39,6	−33,0	−27,9	−23,8	−20,4	−17,6
$2 MnS + 1{}^1/_2 O_2 + H_2O = 2 MnO + H_2S + SO_2$	−162,1	−135,1	−114,3	−99,5	−87,2	−77,2	−68,9	−62,0
$2 MnS + 2 O_2 + H_2O = Mn_2O_3 + H_2S + SO_2$	−421,0	−351,5	−300,0	−260,3	−228,7	−203,2	−182,0	−164,1
$2 MnS + 3 O_2 + H_2O = Mn_2O_3 + 2 SO_2 + H_2$	−327,5	−271,0	−229,2	−197,1	−171,5	−151,1	−133,7	−119,3
$2 MnS + 2 O_2 + H_2O = Mn_2O_3 + SO_2 + H_2 + {}^1/_2 S_2$	−193,5	−159,3	−134,2	−114.8	−99,5	−86,3	−76,8	−68,2
$2 MnS + 2{}^1/_2 O_2 + H_2O = 2 MnO_2 + H_2S + SO_2$	−223,3	−179,5	−147,0	−123,0	−102,2	−86,1	−72,9	−61,7
$2 MnS + 2{}^1/_2 O_2 + H_2O = 2 MnO_2 + SO_2 + {}^1/_2 S_2 + H_2$	−197,5	−159,1	−130,7	−108,9	−91,6	−77,7	−66,1	−56,4
$3 MnS + O_2 + H_2O = 3 MnO + H_2S + S_2$	−74,6	−62,8	−54,1	−47,4	−42,1	−37,8	−34,4	−31,5
$3 MnS + 1{}^1/_2 O_2 + H_2O = Mn_3O_4 + 1{}^1/_2 S_2 + H_2$	−113,5	−92,9	−77,6	−65,9	−56,7	−49,2	−43,0	−37,8
$3 MnS + 2 O_2 + H_2O = 3 MnO + SO_2 + S_2 + H_2$	−182,5	−153,8	−132,5	−116,1	−103,1	−92,6	−83,8	−76,5
$3 MnS + 2 O_2 + 2 H_2O = Mn_3C_4 + 2 H_2S + SO_2$	−209,0	−170,2	−141,4	−119,2	−101,6	−87,4	−75,6	−65,7
$3 MnS + 2{}^1/_2 O_2 + H_2O = 3 MnO_2 + H_2S + S_2$	−166,4	−129,5	−102,1	−81,2	−64,6	−51,5	−40,0	−30,7
$3 MnS + 2{}^1/_2 O_2 + H_2O = Mn_3O_4 + SO_2 + S_2 + H_2$	−503,7	−422,5	−363,9	−316,1	−279,3	−249,4	−224,7	−203,9
$3 MnS + 4{}^1/_2 O_2 + H_2O = Mn_3O_4 + 3 SO_2 + H_2$	−534,8	−446,7	−381,5	−331,3	−291,3	−259,0	−232,1	−209,0
$4 MnS + {}^1/_2 O_2 + H_2O = 4 Mn + H_2S + SO_2 + S_2$	+317,1	+263,3	+223,5	+192,9	+168,6	+148,8	+132,3	+118,4
$4 MnS + 1{}^1/_2 O_2 + 3 H_2O = 2 Mn_2O_3 + 3 H_2S + {}^1/_2 S_2$	−107,3	−82,9	−65,0	−51,2	−40,3	−32,0	−24,4	−18,4
$4 MnS + 2{}^1/_2 O_2 + H_2O = 4 MnO + H_2S + SO_2 + S_2$	−254,6	−213,1	−182,4	−158,8	−140,0	−124,7	−112,0	−101,3
$4 MnS + 3{}^1/_2 O_2 + H_2O = 2 Mn_2O_3 + H_2S + SO_2 + S_2$	−368,9	−302,6	−253,5	−215,7	−185,7	−161,4	−141,3	−124,4
$4 MnS + 4{}^1/_2 O_2 + H_2O = 4 MnO_2 + H_2S + SO_2 + S_2$	−377,0	−302,3	−246,6	−203,9	−170,1	−142,6	−119,3	−100,8
$6 MnS + 2 O_2 + 4 H_2O = 2 Mn_3O_4 + 4 H_2S + S_2$	−150,6	−117,8	−93,5	−74,9	−60,1	−48,2	−38,4	−30,2
$6 MnS + 4{}^1/_2 O_2 + H_2O = 2 Mn_3O_4 + H_2S + SO_2 + 2S_2$	−478,3	−393,6	−330,9	−282,6	−244,2	−213,2	−187,3	−165,7

hydrogen sulfide from power-producing gas at 1000°C. and above should be carried out by use of alkaline earth metal oxides. At 600-800°C., the solid reactants used may be iron oxides or manganese oxides. In this connection it became necessary to determine the activity of oxides of the indicated metals of this group relative to hydrogen sulfide at high temperatures. The activity of the solid reactants was studied in a medium of pure hydrogen sulfide and in its mixture with water vapor.

The study using alkaline earth oxides was carried out on an assembly with continuous automatic recording of kinetic curves obtained from the change in the volume of the escaping gas (Fig. 8).

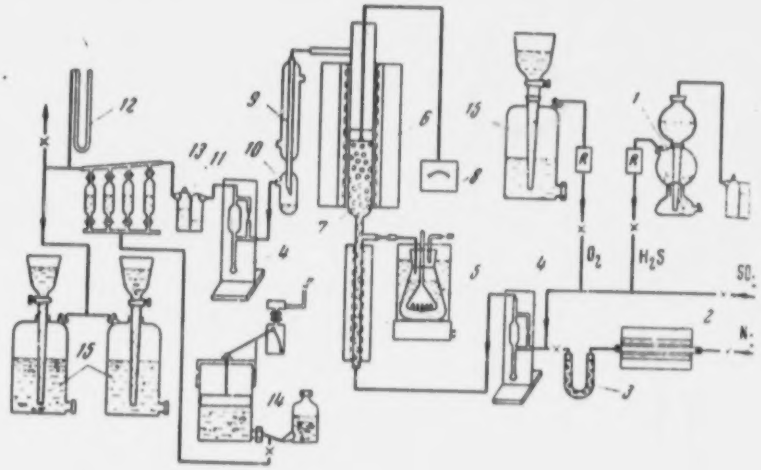


Fig. 8. Diagram of experimental assembly.

The assembly consisted of a quartz reactor *7* 18 mm in diameter, a condenser *9*, with a float device *14* for recording the volume of the gas which passed through it in reference to time. The unit was first purged with nitrogen from which oxygen had been removed by means of copper turnings *2* and which had been dried with calcium chloride *3*. Weighed amounts of different solid reactants with a particle size of 0.25-0.5 mm were charged on a layer of porcelain particles of the same fraction. The weight of the charge was 0.825 g. The quartz reactor was heated with a demountable electric furnace *6* to a given temperature, then a Kipp generator *1* was used to supply hydrogen sulfide, obtained by reacting hydrochloric acid with ferrous sulfide. The temperature of the layer was measured with a platinum/platinum-rhodium thermocouple connected to a galvanometer. When a steam-gas medium was used, water vapor was supplied from a steam superheater *5*. The unreacted amount of water vapor was condensed in a condensate collector *10*. The amount of gas leaving the quartz reactor was measured with a flow meter *4*. The unreacted hydrogen sulfide was absorbed in alkali in a gas-washing Tishchonko bottle *11*, and the remaining gas was collected at different time intervals into gas-absorption pipets *13* through a U-shaped water manometer *12* with simultaneous measurement of its amount by a float recorder. The velocity of the drum was 69.7 mm/min. A 1 mm vertical displacement of the recorder pen takes place when 9.3 cm^3 of gas is evolved. A large amount of gas was collected periodically into gasometers *15*.

The degree of conversion of hydrogen sulfide was calculated from the amount consumed by the reaction. The amount of unreacted hydrogen sulfide was calculated from the difference between the volumes of the readings of the flow meter and automatic recorder. Knowing the amount of hydrogen sulfide supplied at a given time and the unreacted amount, one can calculate the amount of hydrogen sulfide consumed in the reaction. The degree of conversion of hydrogen sulfide was calculated as the ratio of the amount of H_2S consumed in the reaction to the total amount of hydrogen sulfide supplied during a given period of time.

In order to study the activity of hydrogen sulfide with solid reactants metal oxides were used: calcuim oxide, magnesium oxide, their mixture (50% each), and kaolin. Experiments on the comparative activity of different reactants showed that the most effective reactant with hydrogen sulfide at 1100°C., a linear velocity of 0.099 cm/sec and an actual contact time of 1.56 sec was calcium oxide and a mixture of calcium oxide and magnesium oxide (50%). For these reactants, the degree of conversion of hydrogen sulfide remains a constant equal to 100%, in the course of 30 min (Fig. 9).

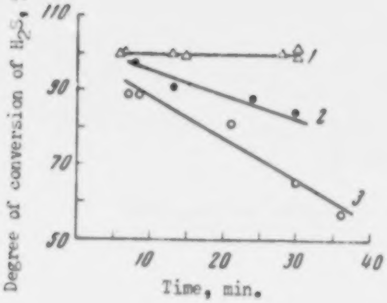


Fig. 9. Comparative activity of different reactants in reactions with pure hydrogen sulfide at 1100°C.

1 - CaO, MgO + CaO; 2 - Kaolin; 3 - MgO.

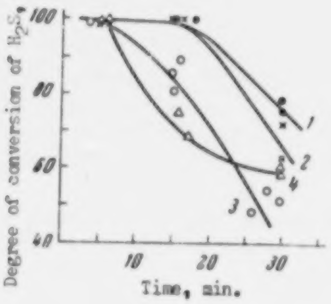


Fig. 10. Comparative activity of reactants in reactions of a mixture of hydrogen sulfide with water vapor at 1100°C.

1 - CaO; 2 - Kaolin; 3 - MgO; 4 - CaO + MgO

Kaolin and magnesium oxide react less actively with hydrogen sulfide. The degree of conversion of hydrogen sulfide after 13 min for kaolin is 91.1%, and after 30 min decreases to 84.4%, whereas for magnesium oxide after 8 min the degree of conversion of hydrogen sulfide reaches 88.5%, then decreases to 66.0% in the course of 30 min.

A study of the activity of solid reactants with hydrogen sulfide (3.06%) in excess water vapor at 1100°C., a linear velocity of the steam-gas mixture equal to 0.032 m/sec and an actual contact time of 0.218 sec shows that calcium oxide is one of the most effective reactants in the reaction with hydrogen sulfide.

The degree of conversion of hydrogen sulfide, equal to 100%, lasts for 16-18 min, and after 30 min drops to 75-78% (Fig. 10). The activity for kaolin in the reaction with hydrogen sulfide in a medium of water vapor is very high, equal to 100% for 15 min, and decreases to 64.4% after 30 min. A mixture of magnesium oxide and calcium oxide (50%), and also magnesium oxide are less active: a 100% conversion of hydrogen sulfide is observed only for 5.5 min, and after 30 min decreases to 60-62% for the mixture and to 48% for magnesium oxide.

Experiments involving the study of the activity of hydrogen sulfide toward alkaline earth metal oxides in a medium of hydrogen sulfide and in a mixture with water vapor showed that the most effective reactant at 1100°C. is calcium oxide. This is a relatively cheap reactant, since it can be obtained by roasting from universally distributed natural limestones. The high reactivity of calcium oxide toward different sulfur compounds is well known. This property is used in technology: the use of limestone for tying up sulfur in metallurgical processes during the melting of pig iron has been widely adopted.

In order to obtain sulfur free metal, the sulfur is converted from iron sulfides into calcium sulfide, which is practically insoluble in the metal, but dissolves well in slags, particularly basic slags. The desulfuration of pig iron with calcium oxide is carried out at high temperatures which cause the sulfur to be eliminated with the liquid slags [20].

In the technology of removal of sulfur compounds from gases, calcium oxide has been used relatively little, mainly in the removal of sulfur dioxide from gases.

In dry methods of hydrogen sulfide removal from gases by means of bog ore, lime is frequently used as the active additive to the ore.

All attempts known thus far to use calcium oxide for the removal of hydrogen sulfide from gases have been random in character, and there are no systematic published studies of the conditions under which this reaction takes place. In this connection, it becomes necessary to make a detailed study of the kinetics of the reaction between hydrogen sulfide and calcium oxide, which takes place both independently and together with side reactions that are possible under such conditions.

As already noted, the use of calcium oxide for purifying sulfur-containing gases is desirable at 1000°C.

In selecting the reactants for removing hydrogen sulfide from gases at 600-800°C., it is also necessary to point out the stability of salts of sulfur compounds and the exclusion of the stability of formation of carbonate salts from the carbon dioxide present in the gases being purified. Thermodynamic analyses have shown that oxides of iron and manganese satisfying the technical requirements of high-temperature purification can be used for removing hydrogen sulfide from gases at 600-800°C. In this respect, various natural iron and manganese ores and also other minerals available for use on a large scale are of some interest. The choice of solid reactants is determined by the chemical activity of the interaction of varios ores and minerals with hydrogen sulfide at high temperatures.

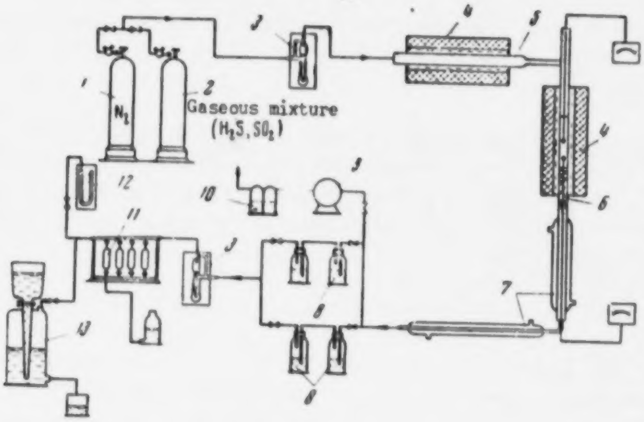


Fig. 11. Diagram of experimental assembly for studying the kinetics reactions of the recovery of sulfur compounds from gases.

A study of the activity of various solid reactants at temperatures to 800°C. was made on a somewhat modified assembly with continuous recording of the reaction rate in time (Fig. 11). The assembly consisted of a quartz reactor *6* 10-13 mm in diameter heated by a demountable electric furnace *4*, a condenser *7*, a gas heater *5*, a system of Drechsel gas-washers *8*, gas-absorption pipets *11*, an U-shaped water manometer *12*, and a gasometer *13*. The experiments used a layer of solid particles of reactants 0.5-1 mm in size, which were charged on a layer of porcelain particles. The height of the reactants was 100 mm, and the weight of the charges varied from 7.0 to 38 g with the density of the reactants used. The hydrogen sulfide necessary for the experiment was obtained from a Kipp generator by reacting hydrochloric acid with ferrous sulfide, and was pumped by liquefaction at -60°C. into a specially prepared flask of 100 cm^3 capacity, the maximum pressure in which was 25 atm. To study the activity of various reactants with hydrogen sulfide, an artificial gas mixture similar in composition to power-producing gas (but without carbon monoxide) was specially prepared at a pressure of 100 atm. Hydrogen sulfide was pumped in first from a samll cylinder. The composition of the gas in the cylinder was as follows (in %): H_2S 0.35-0.5; CO_2 5.9; H_2 18.9, and N_2 74.7-74.85.

The solid reactants used were natural ores and minerals: magnetite of the Sokolovskiy-Sarbay deposit and from Nizhniy Tagil and Vysokaya Mountain, pyrolusite and manganite from the Nikopol' Deposit, KMA (Kursk Magnetic Anomaly) hematite, chromite, sphalerite (preroasted), siderite (light and gray) of the Bakal'skiy deposit (Urals), limestone and dolomite (roasted and unroasted), magnesite (roasted), and sphene.

The order in which the experiments were carried out was as follows: prior to the experiment, the assembly was purged with nitrogen *1*, and after the desired temperature was reached in the layer of reactant, hydrogen sulfide containing gaseous mixture *2* was supplied to the reactor at a certain rate through flowmeter *3*.

Past the reactor, the bulk of the gas which has passed through gas meter *9* and jar with alkali *10* is vented into the atmosphere, and the other part of the gas for determining its hydrogen sulfide content is passed at a certain rate amounting to 200 cm^3/min through Drechsel gas washers *8* filled with cadmium acetate. The method of determination of hydrogen sulfide with cadmium acetate is applicable when the hydrogen sulfide content ranges from 20-30 mg/m^3 to 10-15 g/m^3. After the experiments were carried out, the weighed samples of reactants were cooled in a stream of nitrogen and subjected to chemical analysis to determine the metal sulfide, sulfate, and total sulfur content. The degree of conversion of hydrogen sulfide was calculated from its amount consumed in the reaction. Two series of investigations were carried out to study the activity of the solid reactants with hydrogen sulfide when the latter was present in concentrations of 0.2 and 0.35-0.5%. The composition of the gas is given above. The experiments were conducted at 700°C., a linear gas velocity of 0.46-0.48 m/sec, and a contact time of 0.2-0.22 sec.

The experiments utilized limestone and dolomite roasted for 5 hr at 1000°C.; sphalerite was roasted at 900°C. Unroasted dolomite showed the highest activity in interaction with hydrogen sulfide. After 40 min of reaction, the degree of conversion of hydrogen sulfide was 98.1%, and after 80 min, it decreased to 94.87% (Table 11). For roasted dolomite, the degree of conversion of hydrogen sulfide after 40 min was 96.57%, and after 60 min, 87.65%. Such a decrease in the degree of conversion of hydrogen sulfide was obviously due to the conditions of preparation of the surface in the course of roasting of dolomite.

Siderite (light) during the initial period of its reaction with hydrogen sulfide in the course of 40 min has a lower degree of conversion that increases from 82.87 to 95%, and then its value remains constant for 90 min. This may be due, on the one hand, to the thermal decomposition of siderite during the initial period of the reaction, and on the other hand, to the reduction of the iron oxides obtained by the active components of the gas (hydrogen) to lower oxides, causing the subsequent increase in the degree of conversion of hydrogen sulfide. Roasted magnesite is reactive during the first 20 min, when the degree of conversion of hydrogen sulfide is 91.37-95.45%, and after 60 min decreases to 49.21-51.25%.

Table 11.

Reaction of Hydrogen Sulfide (0.2%) with Different Solid Reactants

(v = 0.47 m/sec; r = 0.21 sec).

Magnesite (roasted)		Light siderite (Bakal, Urals)		Dolomite (roasted)		Dolomite (unroasted)	
I	II	I	II	I	II	I	II
20	95,45	10	82,87	20	98,33	20	98,93
30	37,14	20	91,37	40	96,57	40	98,08
40	73,52	30	93,0	50	87,33	60	95,61
50	65,37			60	87,65	80	94,87
60	49,21	70	96,64	70	77,41	—	—
		90	94,73				

Note. 1 - time, min; 2 - degree of conversion of H_2S, %.

Figure 12 gives the results of studies of the reactivity of various natural ores and minerals with hydrogen sulfide at 700°C. and a hydrogen sulfide concentration of 0.35-0.5%. The greatest effectiveness relative to hydrogen sulfide is shown by pyrolusite MnO_2, KMA hematite Fe_2O_3, magnetite of the Sokolovskiy-Sarbay deposit Fe_3O_4, siderite (gray) $FeCO_3$, and dolomite $CaMg(CO_3)_2$. For these reactants, the degree of conversion of hydrogen sulfide is 97-98% during a long period of purification of the gas. For example, the indicated degree of conversion of hydrogen sulfide for pyrolusite remains constant for 120 min of the reaction, 141 min for magnetite, 90 min for siderite (gray), and 70 min for dolomite (unroasted).

The removal of hydrogen sulfide from the gas by manganite of the Nikopol' deposit [$MnO_2Mn(OH)_2$] is 96.66-98.8% in the course of 60 min, then a decrease to 92.6% is observed after 80 min, and a drop to 66.14% in the course of 100 min of reaction. A lower activity with hydrogen sulfide is shown by magnetite (Nizhniy Tagil), roasted limestone (CaO) and sphalerite (ZnS), followed by limestone and chromite, which has almost no purifying effect.

In the study of the activity of various solid reactants, the composition of the gas in the course of removal of hydrogen sulfide was investigated. As is evident from Table 12, in the reaction of solid reactants with hydrogen sulfide, a change occurs in the composition of the gas being purified, in the direction of a decrease in the carbon dioxide content of the initial gas, and the appearance of carbon monoxide and water vapor is observed in the final gas. Such a change of the composition is due to the occurrence of the reaction $CO_2 + H_2 \rightleftarrows CO + H_2O$.

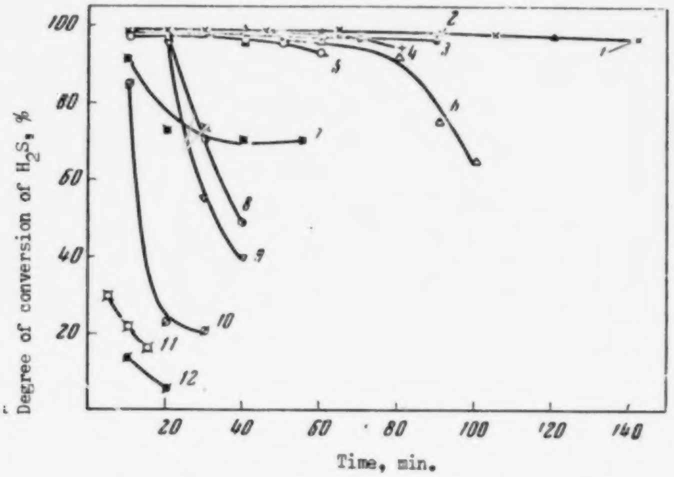


Fig. 12. Change in the degree of conversion of hydrogen sulfide with time in reactions with different substances at 700°C., for a velocity of 0.48 m/sec, and a time of 0.21 sec.

1 - magnetite of Sokolovskiy-Sarbay deposit; 2 - pyrolusite of Nikopol' deposit; 3 - gray siderite; 4 - unroasted dolomite; 5 - light siderite; 6 - manganite of Nikopol' deposit; 7 - magnetite of Nizhniy Tagil deposit; 8 - roasted limestone; 9 - roasted sphalerite (ZnS); 10 - limestone; 11 - sphene; 12 - chromite;

It is evident that at 700°C. the reconversion reaction $CO_2 + H_2$ takes place on all the solid reactants used.

Thus, analysis of results of the study of the activity of solid reactants with hydrogen sulfide showed that the most effective ones at 700 °C. are pyrolusite, hematite, magnetite, siderite, and dolomite. These reactants may be used in the technology of hydrogen sulfide removal from gases at 600-800°C. In order to obtain a definitive evaluation of the use of these reactants in the removal of hydrogen sulfide from gases, it is necessary to study the optimum conditions of recovery of sulfur compounds from combustible gaseous mixtures. In this regard, iron and manganese ores, which we shall discuss in more detail below, are of definite interest for the study.

Table 12.

Change of the Gas Composition during the Reaction of Hydrogen Sulfide (0.35-0.5%) with Solid Reactants.

Reactant	Initial gas, vol. %					Final-gas, vol. %			
	H_2S	CO_2	H_2	N_2	Time, min	CO_2	CO	H_2	N_2
Magnetite									
Sokolovskiy-Sarbay	0,37	5,7	18,9	75,33	141	4,63	2,4	18,28	74,67
Nizhniy Tagil	0,34	5,4	18,9	75,33	55	4,60	2,1	16,05	77,22
Nikopol' pyrolusite	0,35	5,4	18,9	75,33	60	3,50	3,0	16,10	77,40
KMA hematite	0,35	5,3	19,7	74,58	60	2,80	2,8	14,65	79,75
Manganite	0,32	5,3	19,7	74,61	100	2,60	3,0	17,33	77,07
Roasted sphalerite	0,44	5,9	17,7	75,96	25	5,00	0,4	15,58	79,02
Siderite									
gray	0,47	5,9	17,7	75,93	40	3,70	1,3	14,90	80,70
light	0,46	5,9	17,7	75,94	28	2,40	3,6	14,75	79,25
Limestone									
roasted	0,46	5,9	17,7	75,94	22	2,49	1,3	9,35	86,86
unroasted	0,50	5,9	17,6	76,00	30	2,50	2,0	10,00	85,50
Unroasted dolomite	0,50	5,9	17,6	76,00	75	3,90	3,0	14,62	78,48

REMOVAL OF HYDROGEN SULFIDE FROM GASES BY MEANS OF CALCIUM OXIDE

Studies of the activity of various solid reactants have established that the most effective absorbent of hydrogen sulfide at 1000-1100°C. is calcium oxide. In order to determine the optimum conditions of the reaction between calcium oxide and hydrogen sulfide at high temperatures, it was necessary to study a large group of problems involved in the practical realization of the process as a whole.

An experimental study of the process was carried out by using a method similar to the one described earlier in experiments designed to evaluate the activity of solid reactants.

A layer of calcium oxide particles from 0.25-0.5 to 2-3 mm in size was used for the experiments. The height of the active layer ranged from 4 to 95 mm.

In work with different hydrogen sulfide concentrations (0.3-1%) in the gaseous mixtures, the latter were obtained by premixing the gases before sending them into the reactor.

The kinetics of the reaction of hydrogen sulfide with calcium oxide were studied in a neutral nitrogen medium with different concentration of hydrogen sulfide in the gaseous mixture.

The study established that as the velocity of the blast increases, the rate of absorption of hydrogen sulfide by calcium oxide increases linearly (Fig. 13).

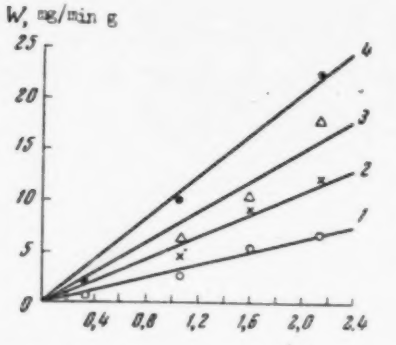


Fig. 13. Rate of reaction of H_2S present in different concentrations with calcium oxide versus velocity of the blast (time from start of experiment 30 min, temperature 1000°C., fraction 1-2 mm).
1 - 0.2%; 2 - 0.3%; 3 - 0.4%; 4 - 0.5%

Under the conditions of the experiments, which were technically limited by the magnitude of the possible velocity of the blast (2.13 m/sec), we were unable to exclude the influence exerted on the reaction rate by the diffusion inhibition associated with the flow of the reacting mixture to the surface of the solid material. This indicates that the reaction in question can have a much higher rate if a kinetic regime of the process is provided for.

For a hydrogen sulfide concentration in the gases up to 0.5 vol. %, characteristic of gaseous hydrogen sulfide-containing mixtures usually subjected to purification, a nearly 100% removal of hydrogen sulfide from the gas is obtained in one hour at a blast velocity up to 2.2 m/sec ($\tau = 0.04$ sec). As the hydrogen sulfide concentration increases from 0.2 to 0.5%, its conversion rate increases (Fig. 14). This obviously corresponds to a steady diffusion regime of the reaction of calcium oxide with hydrogen sulfide, which is first order with respect to the concentration. The degree of conversion of hydrogen sulfide with increasing blast velocity at different concentrations (0.2--0.5%) remains relatively high and at the given height of the layer amounts to 99-100% in the course of one hour.

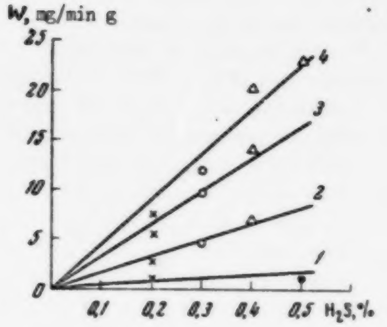


Fig. 14. Rate of the reaction of H_2S with CaO versus H_2S concentration at different velocities of the blast (time from start of experiment 30 min, temperature 1000°C., fraction 1-2 mm).

1 - 0.32 m/sec; 2 - 1.06 m/sec; 3 - 1.6 m/sec; 4 - 2.13 m/sec.

The influence of temperature on the rate of absorption of hydrogen sulfide by calcium oxide was studied at a linear velocity of the gas feed of 2.13 m/sec and a hydrogen sulfide concentration of 0.3%. The temperature was varied from 500 to 1000°C. The highest degree of conversion of hydrogen sulfide, 99-100%, in the course of one hour was observed at 500 and 700°C. The decrease of the degree of conversion of H_2S during the same period was respectively equal to 71.2 and 54.8 (Fig. 15).

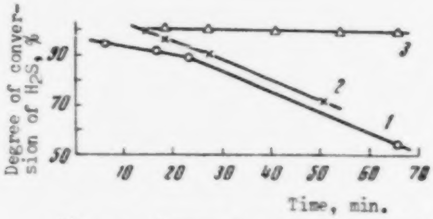


Fig. 15. Degree of conversion of H_2S versus temperature (blast rate 2.13 m/sec, contact time 0.039 sec).

1 - 500°C.; 2 - 700°C.; 3 - 1000°C.

The value of the activation energy (Fig. 16) was 3300-4500 cal/mole, which confirms the diffusional character of the process of sulfur removal under the conditions of the experiments.

Studies of the influence of the height of the calcium oxide layer on the reaction rate were conducted in a neutral medium of nitrogen at 1100°C., a linear gas velocity of 0.021 m/sec, a hydrogen sulfide concentration of 4.5%. and a particle size of 0.25-0.5 mm. The height of the layer was varied from 4 to 52 mm. Correspondingly, the amount of calcium oxide in the weighed sample ranged from one-half the stoichiometric amount to a tenfold excess.

It is evident from Fig. 17 that when the height of the layer h = 4 mm (τ = 0.185 sec), the degree of conversion of hydrogen sulfide, equal to 100%, is observed only during the initial period of the reaction and as early as 2.92 min from the start of the reaction drops to 80%. For a layer height h = 35 mm (τ = 1.62 sec), a 100% degree of conversion of H_2S is preserved for 56 min. Thus, under the conditions of the experiments, in order to ensure a 100% conversion of hydrogen sulfide, a minimum time of contact between the hydrogen sulfide-containing gases and pure calcium oxide is required that at v = 0.02 m/sec amounts to 0.2 sec. Other things being equal, for a shorter time of contact between the gases and the solid reactant (decrease of the height of the layer) and a longer residence time of the layer of the indicated height of solid material in the reaction zone (increase of consumption of CaO from the given charge), a breakthrough of hydrogen sulfide is observed, i.e., there is a low degree of conversion of hydrogen sulfide.

It is of interest to evaluate the excess calcium oxide over the stoichiometric amount providing for a 100% conversion of hydrogen sulfide for different heights of the layer. This quantity was calculated from the formula

$$M=\frac{A-gt}{gt}=\frac{A}{gt}-1,$$

where M is the excess calcium oxide over the necessary stoichiometric amount; A is the weight of the initial charge, mg; g is the stoichiometric amount of CaO reacting completely per unit time with all of the H_2S supplied, mg/min; t is the residence time of CaO in the reaction zone from the start of the reaction, min.

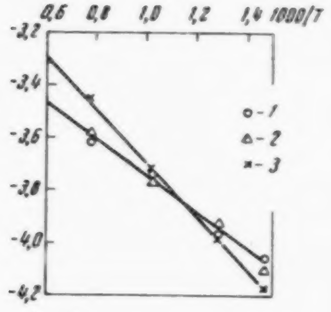


Fig. 16. Logarithm of the rate of the reaction of H_2S with CaO versus 1000/T.
1 - 30 min; 2 - 40 min; 3 - 50 min.

The consumption of calcium oxide at different times is shown in Table 13. As is evident from this table, the minimum excess of calcium oxide is 10-12, when a 100% conversion of hydrogen sulfide is maintained, and below this value a lower degree of conversion and a breakthrough of hydrogen sulfide are observed. Hence, for the indicated minimum excess of pure calcium oxide, the degree of consumption of the solid reactant will be 10%. In a process where the calcium oxide excess is greater, the consumption of the solid reactant will always be higher, since the hydrogen sulfide breakthrough in the presence of a calcium oxide excess of less than 10-12 does not signify the elimination of the remaining amount of calcium oxide from the reaction and indicates only its operation with a lower degree of conversion of hydrogen sulfide.

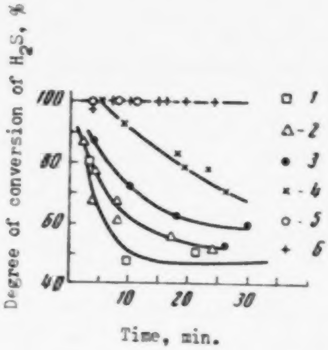


Fig. 17. Effect of layer height on the degree of conversion of hydrogen sulfide reacting with calcium oxide.

$1 - \tau_1 = 0{,}185$ sec $h_1 = 4$ mm; $2 - \tau_2 = 0{,}32$ sec, $h_2 = 7$ mm; $3 - \tau_3 = 0{,}46$ sec; A $h_3 = 10$ mm; $4 - \tau_4 = 0{,}85$ sec, $h_4 = 18$ mm; $5 - \tau_5 = 1{,}62$ sec, $h_5 = 35$ mm; $6 - \tau_6 = 2{,}4$ sec, $h_6 = 52$ mm

At the same time, a 100% conversion of hydrogen sulfide is achieved by a sufficient layer height. This is demonstrated by data obtained in experiments with 100% absorption of hydrogen sulfide and different layer heights, where the degree of consumption of calcium oxide reached 30-35%, and the residence of the solid material in the apparatus was 1 hr.

Table 13.

Consumption of Calcium Oxide Relative to the Stoichiometric Amount for Different Layer Heights (in mm) and Weights (in g).

Time, min	$A_1 = 0{,}407$, $h_1 = 4$	$A_2 = 0{,}815$, $h_2 = 7$	$A_3 = 1{,}635$, $h_3 = 10$	$A_4 = 3{,}26$, $h_4 = 18$	$A_5 = 6{,}0$, $h_5 = 35$	$A_6 = 10{,}0$, $h_6 = 52$
1	10,40	21,80	44,60	90,10	166,50	279,0
4	1,84	4,67	10,40	21,70	40,80	68,7
5	1,28	3,55	8,13	17,20	32,50	54,8
10	0,14	1,28	3,58	8,10	15,70	26,9
15	—	0,52	2,04	5,06	10,15	17,6
20	—	0,14	1,28	3,55	7,38	13,0
30	—	—	0,52	2,03	4,58	8,3

Note. Boldface figures denote values of excess calcium below which the hydrogen sulfide breakthrough is observed.

The dependence of the degree of consumption of CaO on the layer height is shown below:

Layer height of CaO, mm	35	60
Sample weight, g	6	10
Contact time T, arb. sec	0,35	0,6
Linear gas velocity, m/sec	0,021	0,021
Degree of consumption of CaO, %	36,0	21,6

Thus, experiments conducted with different heights of the calcium oxide layer demonstrated the feasibility of a complete conversion of hydrogen sulfide in the presence of a minimum excess of the pure solid reactant, equal to 10-12 as compared with the stoichiometric amount.

Studies of the thermodynamics and kinetics of the reaction of calcium oxide with hydrogen sulfide showed that this process can be carried out in practice at high temperatures (about 1000°C.). The use of such a process is of major interest for certain branches of industry (chemistry, metallurgy), and should be applied to the recovery of hydrogen sulfide from complex gaseous mixtures containing various active gases (H_2, CO, CO_2, H_2O).

Thus it is necessary to analyze the problem of the effect of the composition of gaseous mixtures on the removal of hydrogen sulfide from them by means of calcium oxide at high temperatures.

Thermodynamic analysis showed a possible influence of the main reaction of water vapor and hydrogen on the results, and also a probable occurrence of the reversible reaction of conversion of carbon monoxide by water vapor. The presence of water vapor shifts the equilibrium of the reaction $CaO + H_2S \rightleftarrows CaS + H_2O$ in the opposite direction, i.e., will inhibit the removal of hydrogen in sulfide from gaseous mixtures. The presence of hydrogen in the gas will hinder the reaction of thermal decomposition of hydrogen sulfide $H_2S \rightleftarrows H_2 + {}^1/_2\, S_2$, which is undesirable in the purification of gases, since it is associated with the evolution of elemental sulfur.

Experiments on the effect of water vapor on the rate of the reaction $CaO + H_2S$ were carried out at 1100°C., with the charging of 0.815 g of calcium oxide having a particle size of 0.25-0.5 mm, and a linear velocity of the steam-gas mixture of 0.08 and 0.1 m/sec. The concentration of hydrogen sulfide was 0.94 and 1.26%, and that of water vapor, 98.74-99.06%. To compare the results obtained, the experiments were conducted under the same conditions, but in a neutral medium of nitrogen. It is evident from Table 14 that the degree of conversion of hydrogen sulfide in the neutral medium is 100% during a long period of time (70 min). At the same time, in a medium of water vapor in the presence of the same low concentration of hydrogen sulfide, other conditions being equal, a 100% conversion is observed only during the initial period (6 min). After 30 min, the conversion of hydrogen sulfide decreases to 30-60%.

Table 14.

Effect of Water Vapor on the reaction $CaO + H_2S = CaS + H_2O$ ($t = 1100°C$; 0.25-0.5 mm fraction).

H_2S, %	N_2, %	H_2O, %	Linear velocity, m/sec	Contact time τ, sec	Reaction time, min	Degree of conversion of H_2S, %	Degree of decomposition of H_2O, %
1,26	—	98,74	0,08	0,09	6,5	100,0	0,016
					17,0	87,8	0,940
					30,0	60,7	1,050
1,26	—	98,74	0,08	0,09	6,0	100,0	0,097
					16,0	89,0	0,760
					30,0	60,9	0,860
0,94	—	99,06	0,10	0,07	6,0	100,0	0,098
					19,0	56,0	0,640
					30,0	28,0	0,820
0,94	—	99,06	0,10	0,07	6,0	100,0	0,027
					17,0	50,0	0,480
					30,0	31,9	0,790
1,00	99,0	—	0,10	0,08	3,0	100,0*	—

*Under these conditions and for a reaction time of 9-70 min., the degree of conversion of H_2S continued to remain equal to 100%.

The series of experiments performed clearly show that the degree of conversion of hydrogen sulfide in the presence of a large excess of water vapor (up to 100-300) may decrease substantially, but in practice, the purification of gases is usually achieved with a much smaller excess of steam (20-40).

In the experiments, the degree of decomposition of water vapor was low and amounted to 0.1-1%. Possible secondary reactions taking place with the formation of calcium sulfate are almost absent here. This is also confirmed by chemical analysis of the solid residue.

Thermodynamic analysis showed that the thermal decomposition of hydrogen sulfide substantially affects the results of the process only at temperatures above 1200-1300°C. Up to 1100°C., the thermal decomposition of hydrogen sulfide at equilibrium does not exceed 10%.

The reaction of thermal decomposition of hydrogen sulfide is inhibited even at a relatively low content of hydrogen in the blast. To confirm this and to follow the effect of hydrogen on the degree of thermal decomposition of hydrogen sulfide, the experiments were conducted in a hollow quartz reactor 20 mm in diameter at a linear velocity of the nitrogen-hydrogen mixture of 0.53 m/sec, at 1000°C., and with the following composition of the gas supplied (in %): H_2 15.2, N_2 84.43, and H_2S 0.37. After the gas mixture was passed several times through the heated hollow quartz reactor with porcelain packing of the 2-3 mm fraction and a height of 35 mm, the hydrogen sulfide content at the exit from the reactor was the same (0.37%) as at the entrance. This confirms the thermal stability of hydrogen sulfide in the presence of hydrogen. The presence of hydrogen in the gaseous mixture excludes the thermal decomposition of hydrogen sulfide with the liberation of elemental sulfur and permits one to determine the true rate of the reaction between calcium oxide and hydrogen sulfide.

Experiments showing the effect of carbon dioxide in a gaseous mixture on the rate of the reaction of hydrogen sulfide with calcium oxide were carried out in a quartz reactor 18 mm in diameter with a layer height of 35-41 mm, a particle size of 2-3 mm, at 1000°C., and at a linear gas velocity of 0.1 m/sec. The hydrogen sulfide concentration was 0.35-0.5%; the content of carbon dioxide was 8%, and that of nitrogen, 91.6%.

The results of the study showing the effect of the composition of different gaseous mixtures on the rate of the reaction studied are presented in Table 15. The degree of conversion of hydrogen sulfide was high (99.0%) for 1 hr. This demonstrates that the carbon dioxide present in the gas does not affect the rate of this reaction. In addition, at 1000°C. and in the presence of carbon dioxide in the gas, no visible reaction was observed between the latter and calcium oxide, since the indicated temperature was above the dissociation temperature of calcium carbonate. There is no change in the rate of the direct reaction of hydrogen sulfide with calcium oxide in the presence of carbon dioxide.

The second series of experiments were conducted in order to determine the rate of the reaction with calcium oxide using a hydrogen sulfide-containing mixture of gases close in composition to the power-producing gas obtained from the gasification of sulfur-containing mazuts. The experiments were conducted witha 10-g calcium oxide charge, a layer height of 57 mm, and a particle size of 2-3 mm, at a linear gas velocity of 0.1 m/sec and a temperature of 1000°C. A gaseous mixture of the following composition was used (in %): H_2S 0.36; CO 9.8; CO_2 13.8; H_2 13.0; CH_4 4.4, and N_2 59.0.

It is evident from Table 15 that under the indicated reaction conditions, there is a change in the composition of the gas undergoing purification in the direction of a decrease in the content of carbon dioxide and hydrogen and an increase in the content of carbon monoxide and water vapor. After purification, the gas contained (in %): CO_2 7.07; CO 17.68; H_2 10; CH_4 4.80; and N_2 60.45. Such a change in the gas composition is explained by the occurrence of the reaction $CO_2 + H_2 \rightleftarrows CO + H_2O$.

It is well known that calcium oxide is a catalyst in the conversion reaction $CO + H_2O$. At high temperatures, the reconversion reaction $CO_2 + H_2$ takes place, which is observed under the conditions of the experiments performed.

Table 15.

Reaction of Hydrogen Sulfide with Calcium Oxide versus Composition of Gaseous Mixtures (t = 1000°C.; v = 0.11 m/sec; T = 0.57 sec).

H_2S, vol. %	Composition of initial gas		Reaction time, min	Degree of conversion of H_2S, %	Sulfur residue, mg/m^3	Composition of final gas, %.				
	Component	Vol. %				CO_2	H_2	CO	CH_4	N_2
0,35	CO_2	8,00	10,00	99,63	19,0	7,00	—	—	—	93,00
	N_2	91,65	17,00	99,59	21,0	8,00	—	—	—	92,00
			26,30	99,61	19,8	8,00	—	—	—	92,00
			25,00	99,63	18,5	8,00	—	—	—	92,00
			59,00	99,54	23,4	8,00	—	—	—	92,00
0,36	CO_2	13,80	5,50	97,70	121,0	5,97	7,98	13,98	3,42	68,65
	CO	9,80	11,50	97,60	126,0	6,57	8,38	17,00	5,15	62,90
	H_2	13,00	20,00	97,80	116,0	7,07	10,00	17,68	4,80	60,45
	CH_4	4,40	38,00	97,80	117,0	6,37	9,42	16,63	4,68	62,80
	N_2	59,00	57,83	97,50	134,0	6,43	9,28	17,53	4,93	61,83
0,45	CO_2	6,50	7,00	98,50	102,5	6,55	9,60	16,45	4,30	63,10
	CO	16,45	14,83	98,20	130,5	6,60	8,10	18,50	6,60	60,20
	H_2	9,60	23,00	97,50	173,5	6,90	10,90	18,30	5,30	58,60
	CH_4	4,30	40,50	97,80	145,5	7,10	11,10	18,50	4,80	58,50
	N_2	63,10	62,00	97,60	162,0	7,50	10,70	18,20	5,10	58,50
0,42	CO_2	9,20	7,00	97,50	163,0	4,10	8,70	5,45	3,30	78,45
	H_2	13,10	15,00	97,20	181,0	4,10	8,30	5,90	4,30	77,50
	CH_4	4,30	20,50	96,80	193,5	3,90	10,30	6,40	4,00	75,40
	N_2	73,40	40,30	96,70	203,0	6,72	8,38	5,80	3,40	75,70
			57,50	96,70	210,0	4,50	8,57	6,00	3,79	77,10

To confirm this fact, experiments were carried out with all other conditions being the same, but in the absence of carbon monoxide, using a gaseous mixture of the following composition (%): H_2S 0.42; CO_2 9.2; H_2 13.1; CH_4 4.3, and N_2 73.4. It is shown that in this case the escaping gas contains up to 5.6-5.9% of carbon monoxide which obviously resulted from the reconversion reaction $CO_2 + H_2$.

A change in the composition of the gas obtained in the direction of a decrease of hydrogen and increase of carbon monoxide should not have any appreciable effect on the caloric value of the gas being purified, since the caloric value of the combustible components H_2 and CO is approximately the same.

When an inert gaseous medium is used (see Table 15), the degree of conversion of hydrogen sulfide of complex gaseous mixtures by calcium oxide remains high (97%) for a long period of time (in experiments longer than 1 hr).

Such a high degree of conversion of hydrogen sulfide, obtained in the experiments, indicates a high activity of calcium oxide toward hydrogen sulfide in different gaseous media. The presence of hydrogen lowers the rate of thermal decomposition of hydrogen sulfide and demonstrates a high actual rate of the main process.

As a result of the development of a method of high-temperature removal of hydrogen sulfide from gaseous mixtures by means of calcium oxide, it became necessary to determine the conditions of repeated use of solid reactants in order to determine the possibility of utilizing the recovered sulfur and reducing the consumption of the reactant.

The main objectives were to determine the optimum characteristics of calcium sulfide roasting in an oxygen atmosphere and to evaluate the changes in the indices of the reaction of hydrogen sulfide with calcium oxide obtained after the roasting. It is known that roasting of metal sulfides has been widely applied in metallurgy [22]. A large number of studies have been published in the technical literature dealing with the theory and practice of oxidizing roasting of sulfide ores and concentrates of nonferrous metals such as lead, copper, nickel, zinc, and others. The problems involved in the roasting of calcium sulfide have not been studied thus far, obviously because of a lack of its natural sources.

Thermodynamic analysis established that in the roasting of calcium sulfide in atmospheric oxygen medium at temperatures above 1200°C., the process takes place with the predominant formation of CaO and SO_2. Under these conditions, the formation of $CaSO_4$ and SO_3 is improbable, and the amount of elemental sulfur will be minimal because of the presence of excess air.

First of all, it is necessary to determine the optimum roasting temperature at which the sulfur will be driven out of the solid residue completely, and to establish the conditions of possible sintering of calcium sulfide, due to the exothermic character of the roasting process.

Further, it is necessary to establish the optimum consumption of air in order to obtain the maximum content of sulfur dioxide in the escaping gases that is necessary for the production of sulfur or sulfuric acid.

The reaction of calcium sulfide roasting in an atmospheric oxygen medium was studied on the assembly shown in Fig. 11. The solid reactant used was calcium sulfide that met the RU1061-54 Provisional Technical Specifications of the Ministry of the Chemical Industry. The sulfur content of the calcium sulfide ranged from 18 to 25%. Calcium sulfide was first pressed into pellets with a hydraulic press, then the pellets were ground down to the desired size and sifted into fractions. Particles 1-2 mm in size were used in the experiments, and the layer height was 50-70 mm.

As a result of oxidation of calcium sulfide with atmospheric oxygen, sulfur dioxide passed into the gaseous phase; the dioxide was caught in Drechsel gas washers filled with a titrated iodine solution. Preliminary experiments established that no sulfur trioxide was formed in the gaseous phase.

After the experiment, the weighed sample was cooled in a stream of nitrogen down to room temperature and subjected to chemical analysis to determine calcium sulfide and sulfate and total sulfur in the solid phase.

The reaction of oxidation of calcium sulfide by atmospheric oxygen is exothermic:

$$CaS + 1{,}5\,O_2 = CaO + SO_2 + 118{,}5 \text{ kcal.}$$

The temperature and air flow rate are determining and interrelated factors in this reaction.

On the basis of the conditions of high-temperature hydrogen sulfide removal from the gas by calcium oxide and the subsequent repeated use of the latter, it is desirable to set up the process in such a way as to provide for a uniform roasting of calcium sulfide in the atmospheric oxygen medium without sintering, but with a certain hardening of the outer surface of the fragments.

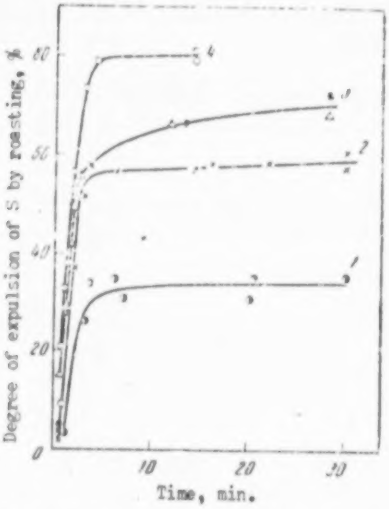


Fig. 18. Change in the degree of expulsion of sulfur by roasting, with time for various initial temperatures of the layer.
1 — 510° C; 2 — 600° C; 3 — 700—800° C; 4 — 900° C

Studies on the effects of temperature on the degree of roasting of calcium sulfide in an oxygen atmosphere were conducted at a linear air velocity of 0.32 m/sec for a contact time of 0.19 sec (Fig. 18). The starting temperature of the heating of calcium sulfide ranged from 510 to 900°C.

The most characteristic feature is the fact that as soon as a given temperature is reached in the layer and air is supplied, the temperature rises noticeably and instantaneously because of the exothermic nature of the process, and this causes an increase in the reaction rate during the first few minutes of the reaction with subsequent expulsion of the bulk of the sulfur by roasting. At t_{in} = 510°C., because of the exothermic nature of the reaction, the maximum temperature in the layer is 1120°C., for t_{in} = 600°C., t_{max} = 1180°C., and for t_{in} = 800-900°C., t_{max} = 1400°C. As a result

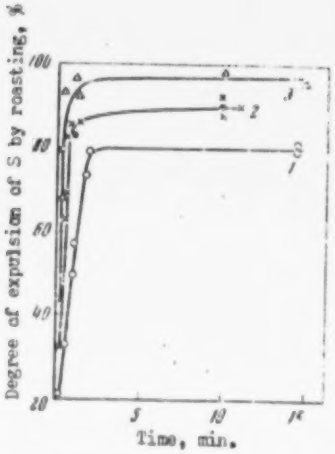


Fig. 19. Change in the degree of expulsion of sulfur by roasting, with time at various gas velocities.
1 -- v_1 = 0,32 m/sec; τ_1 = 0,19 sec; 2 -- v_2 = 0,52 m/sec, τ_2 = 0,109 sec; 3 -- v_3 = 1,06m/sec, τ_3 = 0,056 sec.

of unsteady conditions, a nonuniform expulsion of sulfur takes place.

During the first 3-3.5 min for t_{in} = 510°C., the roasting reaches 27-34.4%, and 1.2-4.5% of sulfur dioxide is evolved into the gaseous phase (see Fig. 18). The rate subsequently decreases sharply, and after 30 min the degree of expulsion amounts to only 35.6%. At t_{in} = 600-800°C., the roasting process proceeds much more vigorously; in 2.5 min, the degree of sulfur expulsion is already 50-56%. The amount of sulfur dioxide in the gas reaches 10-15%. Then the rate of the entire process slows down sharply. At t_{in} = 900°C., the maximum temperature rises to 1450-1500°C., and in 4 min the roasting proceeds to the extent of 79-80%. In the escaping gas, the sulfur dioxide concentration is 13-15%. During the period of the highest reaction rate, at an excess air coefficient = 1, the highest sulfur dioxide concentration is observed in the gaseous phase, equal to 15%, and at = 1.2-1.5, the sulfur dioxide concentration decreases to 10-12.3%. After the expulsion of the bulk of the sulfur from the solid reactant, the value of the excess air over the stoichiometric amount increases to 7-10, and the rate of roasting still remains insignificant. The low reaction rate at the end of the roasting is due to the transition into the regime of the internal diffusion region.

In a practical realization of the process of roasting of calcium sulfide in an atmospheric oxygen medium, it is evident that at a slow reaction rate the amount of air supplied should be decreased.

Studies made on the roasting of calcium sulfide in atmospheric oxygen show that a vigorous roasting takes place at 1200-1400°C., which corresponds to an initial layer temperature of 850-900°C.

The choice of temperature for setting up a steady roasting process for the purpose of high-temperature removal of hydrogen sulfide from the gas may be made by considering the entire set of conditions - flow rate of air and amount of sulfur to be roasted.

In order to study this phenomenon, the experiments were conducted by using linear air velocities v_1 = 0.32 m/sec, v_2 = 0.52 m/sec, and v_3 = 1.06 m/sec at an initial layer temperature of 900°C. As the air blast velocity increases from 0.32 to 1.06 m/sec and the contact time decreases from 0.19 to 0.056 sec, the degree of roasting increases, indicating that the roasting rate is determined by external diffusional factors involved in

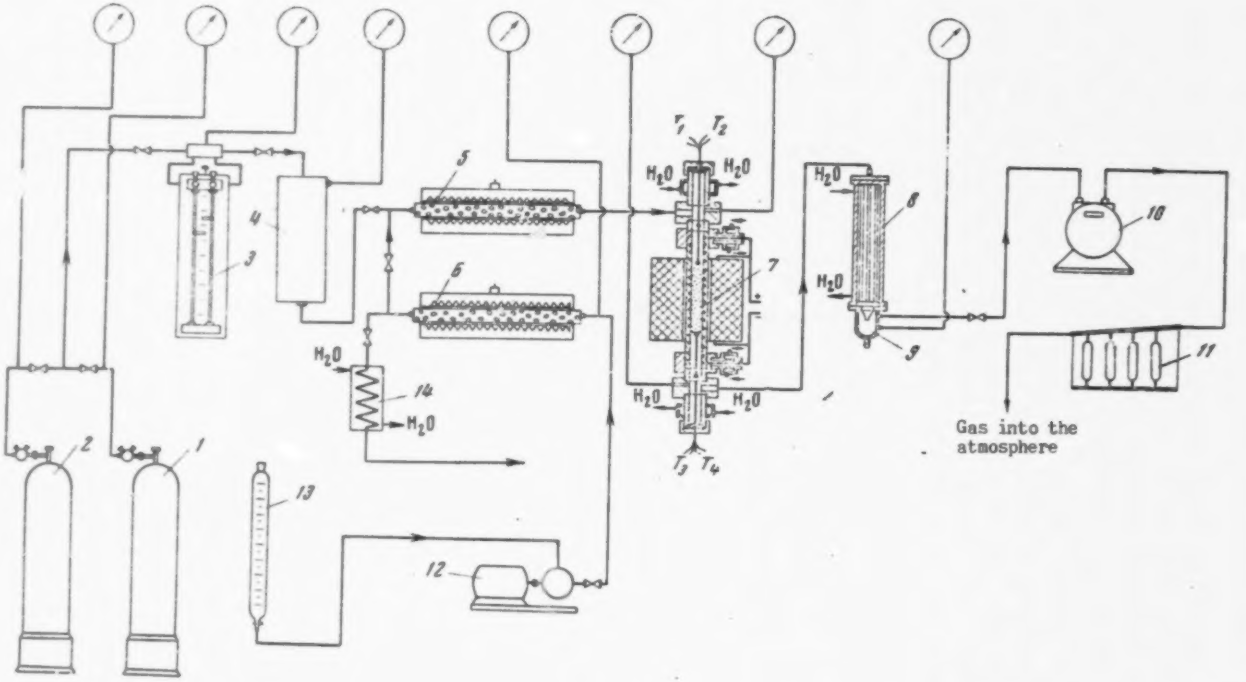

T_1
T_2
H_2O
H_2O
H_2O
H_2O
H_2O
H_2O
H_2O
H_2O
T_3
T_4
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Gas into the atmosphere

Fig. 20. Diagram of assembly for high-temperature removal of hydrogen sulfide from gas under pressure.

the migration of the oxidant to the surface of calcium sulfide (Fig. 19).

The increase in the blast rate affects most noticeably the degree of roasting during the first 1-2 min of the reaction. During this period, the degree of roasting of calcium sulfide at a blast velocity of 0.32 m/sec is 56%, whereas at 0.52 m/sec it reaches 86%, and at 1.06 m/sec, 95-97%. This increase in the degree of roasting of calcium sulfide is due to an increase in the rate of supply of the oxidant to the surface of the reactant and also to the temperature elevation, resulting from the exothermic character of the reaction, which determines the rate of expulsion of sulfur. The maximum temperature in the layer at a blast velocity of 0.32 m/sec is 1160°C.; at 0.52 m/sec it increases to 1200-1300°C., and at 1.06 m/sec, it reaches 1600°C.

The effect of such high temperatures during roasting of calcium sulfide in an atmospheric oxygen medium did not cause any appreciable sintering of the particles; only a certain fusion of the surface was observed, apparently due to the short duration of this action.

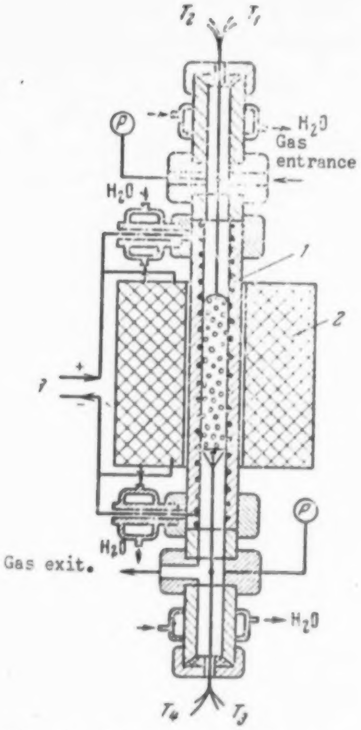


Fig. 21. Diagram of high-temperature reactor for operation under pressure. 1 - inner furnace; 2 - outer furnace; 3 - electric heating.

During the period of maximum roasting rate, a considerable amount of sulfur dioxide is evolved. The sulfur dioxide concentration in the gaseous phase is 12-15%, which corresponds to an excess air coefficient of 1.2-1.3. The sulfur dioxide concentration obtained is sufficient for use in the production of sulfuric acid.

The roasted calcium oxide can be recycled into the process of hydrogen sulfide removal from the gas for multiple use. Thus, the above experiments on the roasting of calcium sulfide showed that a degree of roasting of 95-97% may be achieved at 1200-1400°C. and an excess air coefficient equal to 1-1.2. The concentration of the sulfur dioxide formed in the gas reaches 9-15%.

In order to make a definitive determination of the conditions of the roasting process in the removal of hydrogen sulfide from power-producing gas, it was necessary also to study the repeated use of the solid reactant followed by its regeneration, taking into account the characteristics of the process.

Considering that when a high-temperature removal of H_2S from gas is used at thermal electric power plants, a pressure of 8 and 20 gauge atmospheres is specified for the process, it becomes necessary to use the calcium oxide repeatedly in the course of sulfur removal from the gases under pressure. The study of the high-temperature removal of hydrogen sulfide from the gas by roasted limestone under pressure, followed by regeneration of calcium sulfide by air, was conducted by using the assembly shown in Fig. 20.

The assembly consists of gas heater *5*, steam superheater *6*, reactor *7*, and condenser *8*.

Preliminary experiments established that a substantial loss of hydrogen sulfide from the gas is observed in the hollow reactor, because of metal corrosion. A reactor of special design was constructed for this purpose (Fig. 21).

An alloy spiral 2 was wound on a porcelain tube 17.5 mm in diameter and 1 m long and was placed in a stainless steel jacket with an inner diameter of 50 mm and outer diameter of 60 mm. Between the porcelain tube and the steel jacket was packed a layer of grog brick charge with a particle size of 0.5-0.6 mm, and at the exit from the tubes the ring-shaped charge was coated with kaolin.

The contacts were brought out by using insulation material teflon (polytetrafluoroethylene), which withstands temperatures up to 350°C. and is cooled with water.

On the outside, the reactor was heated with a demountable electric furnace. The solid reactant used was calcium oxide obtained by roasting natural limestone for 5-9 hr at 1100°C. The chemical composition of limestone (%) is given below:

SiO_2	1,92	MgO	1,04
Al_2O_3	0,67	SO_3	0,11
Fe_2O_3	0,58	Calcination loss	42,42
CaO	52,6		
		Total	99,36

The hydrogen sulfide-containing gaseous mixture was specially prepared under a pressure of 100-110 g atm. The height of the active layer ranged from 80 mm to 610 mm. The temperature was measured along the height of the layer at four points at the center of the layer, and in the upper and lower parts, the thermocouple entered to a depth of 10-15 mm. The fourth thermocouple measured the temperature of the entering gas from above.

Prior to the experiment, the entire system was purged with nitrogen *1* (see Fig. 20). After the desired temperature was reached in the layer, a gaseous mixture *2* was supplied from a cylinder with a hydrogen sulfide concentration of 0.2-0.8% through a DT-150 differential manometer *3*, buffer *4*, heater *5*, and into reactor *7*, where the necessary pressure was produced. On leaving the reactor, the gas was cooled in condenser *8*, passed through a gas meter, gas absorption pipets, and vented into the atmosphere. Another part of the gas was passed at a certain velocity (200 cm^3/min) through Drechsel gas washers filled with cadmium acetate to determine the hydrogen sulfide concentration. In work with water vapor, a certain amount of water is supplied from buret *13* by means of pump *12* into steam superheater *6* and enters together with the gas into steam heater *5*. In the calibration of the boiler, the steam condenses in condenser *14* and is collected in receiver *9*. The bulk of the gas then passes through gas meter *10* and is vented into the atmosphere, and the other part is taken up by the gas absorption pipets *11*.

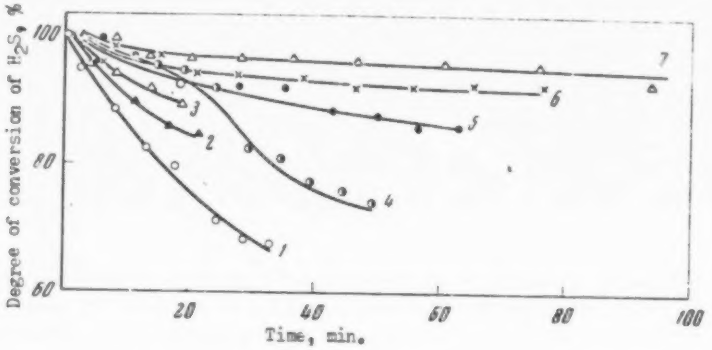


Fig. 22. Change in the degree of conversion of hydrogen sulfide with time in the reaction of CaO and H_2S at different pressures.

1, 2 - pressure respectively 1 abs atm and 20 g atm; $v_1 = 4$ m/sec; $\tau_1 = 0.052$ sec; 3,4 - respectively 1 abs atm and 20 g atm; $v_2 = 2.5$ m/sec; $\tau_2 = 0.13$ sec; 5, 6, 7 - respectively 1 abs atm, 8 and 20 g atm; $v_3 = 2.2$ m/sec; $\tau_3 = 0.22$ sec.

The calcium sulfide formed is regenerated by air in the following manner. The assembly is purged with nitrogen, then the heating is turned on. Simultaneously, Drechsel gas washers filled with cadmium acetate for absorption of the hydrogen sulfide evolved are removed, and the consumption of gas since the start of heating to a given temperature of the experiment is recorded. Air is then supplied to the layer at a certain velocity. The concentration of sulfur dioxide in the escaping gas is determined by passing the latter through Drechsel gas washers filled with a titrated iodine solution. After the experiments have been carried out, the charge is cooled in a stream of nitrogen and subjected to chemical analysis to determine the total sulfur and the sulfide and sulfite sulfur.

Initially, it was necessary to observe the effect of pressure on the degree of removal of hydrogen sulfide from the gas at 1000°C. The study of gas purification with roasted limestone was conducted at a pressure of 1 abs atm and 8 and 20 g atm. The weight of the charge was 110-115 g, the particle size, 1-2 mm, and the linear velocity, 2.2, 2.5, and 4 m/sec. The gas composition was as follows (in %): H_2S 0.53; CO_2 11.02; H_2 18.10; N_2 70.35. It is evident from Fig. 22 that as the pressure increased from 1 abs atm to 20 g atm at a linear velocity of 2.2 m/sec and $\tau = 0.22$ sec, the degree of conversion of hydrogen sulfide increased. At a pressure of 1 abs atm, after 36 min, it was 93.34%, and toward the end of the cycle, after 63 min, it decreased to 86.76%. At a pressure of 8 g atm during the first 15 min it was 96%, and after 76 min it decreased to only 92.5%. The highest degree of conversion of hydrogen sulfide (96.4%) occurred at a pressure of 20 g atm during a long purification period lasting 93 min.

An increase in the linear velocities of the hydrogen sulfide mixture supplied and hence a decrease in the contact time leads to a reduction in the degree of conversion of hydrogen sulfide at pressures of 1 abs atm and 20 g atm. As the pressure increases, the degree of consumption of the reactant rises from 17 to 34%.

The experiments performed showed that hydrogen sulfide can be removed from power-plant gas at pressures of 8 and 20 g atm and at a linear gas velocity of 2.2 m/sec with $\tau = 0.22$ sec (without considering the pressure and temperature), with a sufficiently high degree of purification amounting to 93-96% in the course of 1-1.5 hr.

Experiments at pressures up to 20 g atm also established a slight influence of the water vapor content on the removal of hydrogen sulfide from moist gas (12-15%). Results of experiments with moist hydrogen sulfide-containing gas are given in Table 16. The degree of consumption of the solid reactant was 36.5%.

Table 16.

Removal of Hydrogen Sulfide from Moist (12%) Power-Plant Gas
($v = 4{,}25$ m/sec; $\tau = 0{,}052$ sec).

$H_2S = 0{,}51\%$			$H_2S = 0{,}46\%$		
Time, min	Degree of conversion of H_2S, %	Excess CaO.	Time, min	Degree of conversion of H_2S, %	Excess CaO.
6,00	100,00	34,50	3,50	100,00	14,10
9,16	97,84	9,73	4,66	93,75	10,50
11,33	74,96	6,00	7,75	84,64	6,36
16,16	58,43	4,64	12,33	73,52	4,02
20,50	46,33	3,45	17,83	65,38	2,74
25,00	43,43	2,77	22,83	60,84	2,07
30,00	43,96	2,19	27,00	49,64	1,75

Repeated use of calcium oxide in the course of high-temperature removal of hydrogen sulfide from the gas consisted in the alternate interaction of hydrogen sulfide-containing gas with calcium oxide followed by regeneration with atmospheric oxygen of the calcium sulfide formed.

The determining characteristics of the multiple reuse of calcium oxide were first determined.

The studies showed that the degree of conversion of hydrogen sulfide decreases after a triple absorption, due to a change in the initial conditions of the reaction, namely, a decrease in the weight and height of the change and hence in the contact time.

In order to preserve the initial conditions of the reaction, the charge used in several experiments was combined for subsequent cycles of multiple absorption and regeneration. It should be pointed out that during the roasting of calcium sulfide in atmospheric oxygen, as a result of the exothermic character of the reaction, the temperature in the layer rose to 1600°C. and higher, causing sintering of the whole charge. In order to keep the charge from sintering, the initial temperature of the layer should be properly controlled. Under the conditions of the experiments, the initial heating temperature did not exceed 950°C.

The main series of experiments on the repeated use of calcium oxide (roasted limestone) in the course of high temperature removal of hydrogen sulfide from a gas (Table 17) were carried out under the following conditions:

	h, mm	A, g	v, m/sec	τ, sec	H_2S, %
Absorption 1st . .	610	115,0	2,2	0,3	0,40
2nd . .	450	115,3	2,2	0,214	0,09
3rd . .	450	115,0	2,2	0,214	0,50
4th . .	610	163,0	2,0	0,3	0,54
5th . .	400	146,0	2,0	0,2	0,61
6th . .	500	160,75	2,21	0,23	0,615

The temperature of removal of hydrogen sulfide from the gas was 1000-1100°C., and the pressure was 8 g atm. The process of gas purification involved the use of a hydrogen sulfide-containing gaseous mixture of the following composition (in %): H_2S 0.4-0.6; CO_2 7.6; H_2 22.69; N_2 70.11.

The calcium sulfide formed was regenerated with atmospheric oxygen at a linear velocity of 0.7-0.8 m/sec with a contact time of 0.6-0.8 sec at atmospheric pressure.

Table 17.

Repeated use of Roasted Limestone (1-2 mm Fraction) During Hydrogen Sulfide Removal from Gas under Pressure.

Absorption of H_2S					
1	2	3	4	5	6
0,5/100,0	10,0/97,14	5,0/93,0	5,21/97,0	[illegible],85/93,0	5,0/100
10,0/93,3	20,5/97,0	10,0/97,0	15,0/96,3	11,33/93,0	15/99,3
20,0/98,3	30,0/97,0	15,0/97,0	25,0/96,2	18,0/93,0	25/99,2
30,0/97,9	40,0/95,3	21,0/96,0	34,0/95,8	25,00/97,2	35,0/98,7
40,0/98,0	50,0/95,0	35,0/96,0	50,0/95,0	31,50/97,3	46,0/97,8
43,5/98,0	58,0/76,8	50,0/95,0	62,0/95,6	51,50/96,3	60,0/97,3
53,0/99,64	—	60,0/95,0			71,0/95,3
98,5/98,01					81,0/91,0
105,5/85,23					90,0/88,3

Note. Numerator - time (min); denominator - degree of conversion of H_2S (%).

The air was supplied to a layer heated to an initial temperature of 900°C., and subsequently, because of the exothermic character of the reaction, the temperature rose to 1400-1500°C. The roasting of calcium sulfide in atmospheric oxygen was carried out with a large excess of oxygen, since the purpose was to obtain the maximum possible removal of sulfur from calcium sulfide in order to preserve the activity of the latter in the cycle of absorption of hydrogen sulfide from the gas. The linear velocity of the air was 0.7 m/sec, and the contact time, 0.7 sec.

It is evident from Table 17 that after calcium oxide was used 6 times, its activity was preserved. The degree of removal of hydrogen sulfide from the gas was 98% in the first cycle during 100 min, and in the subsequent cycles, 95-96% in the course of 60 min. The degree of consumption of calcium oxide in the first cycles was 28-37%, then decreased to 23%. As far as the composition of the gas being purified is concerned, as was shown earlier in the case of calcium oxide used as the catalyst, at 1000-1100°C. a change occurs in the direction of a decrease in the content of carbon dioxide and hydrogen and increase of carbon monoxide and water vapor. When calcium oxide is used repeatedly, a similar pattern of change in the gas composition is observed during the entire period of the reaction (Table 18). The process of roasting of calcium sulfide in an atmospheric oxygen medium was carried out for a long time, i. e., lasted 3.5-4 hr. Analysis of the solid residue showed the sulfide sulfur content to be 0.11-0.86%. The degree of roasting reached 95-98%.

Table 18.

Change in the Composition of Power-Plant Gas after the Removal of Hydrogen Sulfide with Calcium Oxide (Roasted Limestone).

Experiment No.	Initial gas, vol. %				Final gas, vol. %.			
	H_2S	CO_2	H_2	N_2	CO_2	CO	H_2	N_2
1	[illegible]	6,00	22,79	70,59	2,15	4,40	19,79	73,66
2	0,45	5,40	20,13	74,02	2,00	6,50	13,57	77,93
3	0,53	11,02	18,10	70,35	3,96	8,03	11,65	76,46
4	0,40	7,60	18,90	73,10	[illegible]	5,21	13,00	78,12
5	0,40	7,60	18,84	73,16	2,70	5,70	13,70	77,90
6	0,69	4,00	18,30	77,01	0,70	3,20	15,52	80,58
7	0,50	7,60	22,69	69,21	2,30	6,00	15,80	76,00
8	0,54	7,60	22,69	69,17	1,90	6,20	16,90	74,90
9	0,61	7,60	22,69	69,10	2,70	5,00	16,00	76,30

During the initial periods of roasting, when the solid residue contains a substantial amount of sulfur, 6-8% SO_2 passes into the gaseous phase even in the presence of a large excess of air. During roasting of calcium sulfide in an oxygen atmosphere, a certain fusion of the surface of the reactant is observed, causing an increase in the mechanical strength of the fragments. Whereas in the first two cycles of absorption and regeneration after the dispersal of the charge up to 5% dust is present, this dust is absent from the following cycles, but 0.5-1 and 0.25-0.5 mm fractions appear that are preserved until the end of the 5th-6th use. In addition, the specific gravity of calcium oxide increased after its use in several cycles.

Thus, the above studies of repeated use of calcium oxide in the removal of hydrogen sulfide from power plant gas at a pressure from 1 abs atm to 20 g atm show its activity to be high after the 6th cycle. At a linear velocity of the gas being purified of 2.5 m/sec and a contact time of 0.25-0.3 sec, the degree of purification in the first cycles reaches 97-98% during 1.5-2 hr, and decreases to 95-98% in the following ones. The degree of consumption of calcium oxide is 28.37% and subsequently decreases to 25%.

REMOVAL OF HYDROGEN SULFIDE FROM GASES BY IRON OXIDES

The study of the activity of various solid reactants at 700°C. showed that iron oxides and in particular, natural iron ores are effective absorbers of hydrogen sulfide from gaseous mixtures. Of greatest interest for practical applications are hematite, magnetite, and siderite.

The reaction of iron oxides with hydrogen sulfide in a reducing medium is a complex process. In addition to direct reactions between iron oxides and hydrogen sulfide, it also involves crystallochemical transformations from higher oxides to lower ones and iron, associated with the reduction of the gas by active components - hydrogen and carbon monoxide. The overall process of hydrogen sulfide removal from gases will be determined by the entire set of physicochemical conditions.

The object of study used was KMA hematite. The first group of experiments were conducted at various blast velocities and at 500°C. The particle size was 0.5-1.0 mm, and the height of the active layer, 50 mm. The gas being purified had the following composition (in vol. %): H_2S 0.34-0.37; CO_2 5.52; H_2 20, and N_2 74.11-74.14. The linear velocity of the gas supplied ranged from 0.484 to 4.18 m/sec. The studies were conducted by using the assembly illustrated in Fig. 11.

The experiments showed that at linear velocities above 3.45 m/sec, the rate of absorption of hydrogen sulfide by hematite was no longer dependent on the feed velocity of the gas being purified, i. e., the extrakinetic region of the reaction is reached under these conditions (Fig. 23). The indicated characteristic of the reaction rate was taken for a time of 5-7 min from the start of the experiment, at which the initial reaction conditions underwent little change. As the process proceeded further and the initial conditions changed, there was also a change in the rate of the reaction between hydrogen sulfide and hematite (Table 19).

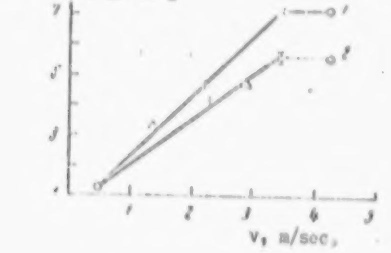


Fig. 23. Rate of the reaction of hydrogen sulfide with hematite versus gas feed rate at 500°C. (0.5-1 mm fraction).

1 - min; 2 - 7 min.

As the blast velocity increases, the degree of conversion of hydrogen sulfide decreases. At blast velocities of 0.48 and 1.36 m/sec, it amounts to 93-96% during 15 min of reaction. At a blast velocity up to 2.18 m/sec, the degree of conversion of hydrogen sulfide is 93.84% in the course of 5 min, and after 20 min it decreases to 26%.

A further increase in blast velocity to 3.44 m/sec leads to a decrease in the degree of conversion of hydrogen sulfide to 77-92% during 4 min and to 16-18.5% during 15 min. At a maximum gas feed velocity of 4.18 m/sec, during 4 min, the degree of conversion of hydrogen sulfide is 87.7%, and during 15 min, 22.14%. The decrease in the degree of conversion of hydrogen sulfide with increasing velocity of the gas being purified is due to a decrease in the time of contact of the gas with particles of the solid reactant.

A study of the effect of temperature on the rate of reaction of hydrogen sulfide with KMA hematite was conducted under conditions similar to those of the extrakinetic region at a linear gas velocity of 3.44 m/sec with particles 0.5-1.0 mm in size. The temperature of the process was 350, 400, 450, and 500°C.

As the temperature rose from 350 to 500°C., the degree of conversion of hydrogen sulfide increased (Fig. 24). At 350°C. it was 41.49% during 2 min of reaction, and during 15 min dropped to 5.45%. At 400°C. it was 48.72% during 3 min and decreased to 16.53% during 15 min.

Table 19.

Effect of Gas Blast Velocity on the Reaction of Hydrogen sulfide with KMA Hematite (t = 500°C.; H_2S, = 0.35%; 0.5-1.0 mm Fraction).

Time, min	Conversion of H_2S, %	Time, min	Conversion of H_2S, %
$v_1 = 4,18$ m/sec	$\tau_1 = 0,012$ sec.	$v_1 = 4,02$ m/sec	$\tau_1 = 0,013$ sec.
3—5	66,16	0—4	87,75
5—9	31,14	4—7	57,68
9—15	22,14	7—10	37,46
		10—13	28,14
$v_2 = 3,46$ m/sec	$\tau_2 = 0,0145$ sec.	$v_2 = 3,41$ m/sec	$\tau_2 = 0,0146$ sec.
0—4	92,50	0—4	75,83
4—7	57,23	4—7	54,05
7—11	23,60	7—10	25,66
11—15	15,65	10—15	18,51
$v_3 = 2,99$ m/sec	$\tau_3 = 0,0167$ sec.	$v_4 = 2,18$ m/sec	$\tau_4 = 0,023$ sec.
0—5	84,82	0—5	93,84
5—7	51,66	5—10	68,68
7—10	43,48	10—15	39,45
10—15	18,51	15—20	26,33
$v_5 = 1,36$ m/sec	$\tau_5 = 0,037$ sec.	$v_6 = 0,484$ m/sec	$\tau_6 = 0,103$ sec.
0—5	96,92	0—3	91,98
5—10	95,90	3—6	91,45
10—15	95,80	6—10	93,06
		10—15	93,36

A temperature rise to 450°C. caused a certain increase in the degree of conversion of hydrogen sulfide; during 3 min it was 59-67.65%, then decreased to 21%. The highest value (89-93.14%) was reached by the conversion of hydrogen sulfide at 500°C. in the course of 3 min of reaction, and during 15 min this value decreased to 25%.

Such a decrease in the conversion of hydrogen sulfide with falling temperature is due to a decrease in the reaction rate under these conditions (Figs. 25 and 26). The values of the reaction rate were calculated by reducing to unity the weights of the actually reacting charge of Fe_3O_4 during certain periods of time during 3, 10 and 15 min, and were referred to the average active concentration of hydrogen sulfide at the given time.

The values obtained for the hydrogen sulfide absorption rate at different times (from the start of the reaction) and at different temperatures are shown in Table 20. The logarithm of the rate of hydrogen sulfide absorption versus the reciprocal absolute temperature is shown in Fig. 27.

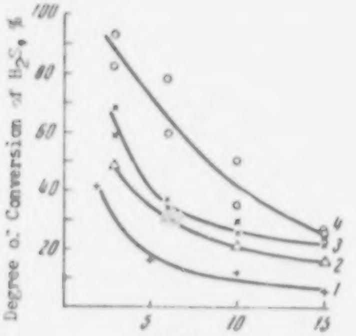


Fig. 24. Effect of temperature on the degree of conversion of hydrogen sulfide in its reaction with hematite (v =3,45 m/sec, τ =0,015 sec, 0.5-1 mm fraction).
1 — 350° C; 2 — 400° C; 3 — 450° C; 4 — 500° C

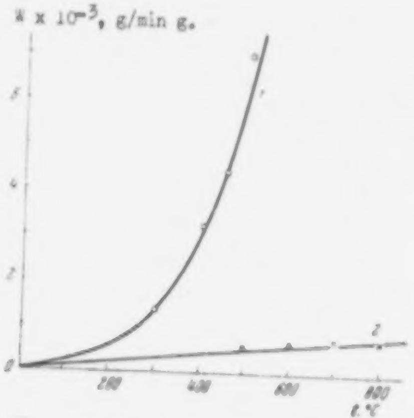


Fig. 25. Effect of temperature on the rate of the reaction of hydrogen sulfide with hematite.
1 — 3,45 m/sec; 2 — 0,69 m/sec

The value of the apparent activation energy determined from Fig. 27 for 3, 10 and 15 min, i. e., for the entire period of the reaction, remained almost unchanged and equal to 8330 cal/mole.

In order to determine the conditions of purification of gases with a high degree of recovery of hydrogen sulfide and during a long period of time, experiments were carried out at elevated temperatures and with a longer contact time. The experiments were carried out at 500, 700 and 800°C. The velocity of the gas supplied was 0.69 m/sec, the contact time 0.15 sec, and the particle size

0.5-1.0 mm. The composition of the gas used was as follows (in %): H_2S 0.34, CO_2 5.83; H_2 19.29, and N_2 74.54. From Table 21 it is evident that a high degree of conversion of hydrogen sulfide was obtained in the experiments at all the temperatures studied,

At 500°C., during the entire period of the reaction (50 min), the gas purification is 96.64-97.65%. A temperature rise to 700-800°C. leads to a certain decrease in the degree of purification to 94-95% in 20 min, and during 60 min it rises to 96-97%. It is obvious that at these temperatures, the reactions of reduction of iron oxides by hydrogen are predominant during the initial period of the process, and thereafter the iron oxides become more reactive with respect to the main process of recovery of hydrogen sulfide from the gases.

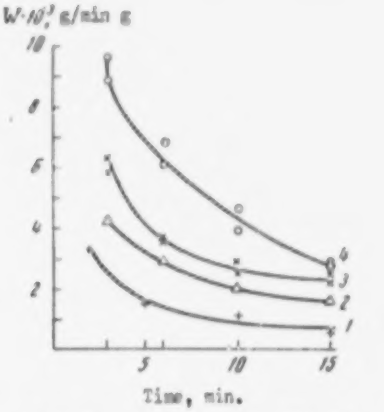


Fig. 26. Change in the rate of the reaction of hydrogen sulfide with hematite in time at different temperatures (v = 3,45 m/sec, τ = 0,015 sec, 0.5-1

1 — 350° C; 2 — 400° C; 3 — 450° C; 4 — 500° C

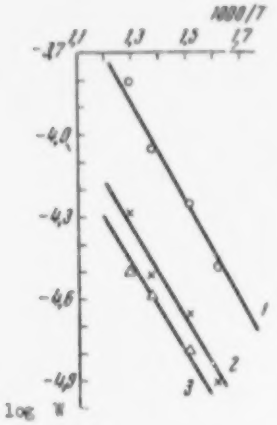


Fig. 27. Logarithm of the rate of the reaction of hydrogen sulfide with hematite versus reciprocal absolute temperature (v = 3,45 m/sec, τ = 0,015 sec, 0,5—1 mm fraction

1 - 3 min; 2 - 10 min; 3 - 15 min.

This is confirmed by the results of analyses of the change of the gas composition with time in the course of purification at different temperatures.

It is evident from Table 22 that the gas composition changes in the direction of a decrease of carbon dioxide and formation of carbon monoxide and water vapor. Moreover, considering that carbon monoxide was absent from the initial gas, such a change in the gas composition may be explained by the occurrence of reactions in which iron oxides are reduced with hydrogen, and also by the development of the reaction between carbon dioxide and hydrogen, $CO_2 + H_2 \rightleftarrows CO + H_2O$. As the temperature rises, the amount of carbon monoxide in the gas increases. It is of interest to evaluate the degree of consumption of hydrogen in reductive reactions of iron oxides and in the reaction of reconversion of carbon dioxide by hydrogen.

Table 22 shows the degree of consumption of hydrogen in the above-indicated reactions at different temperatures. In the first 3-4 min, there is a predominance of reactions of reduction of iron oxides by hydrogen, which take place at different rates at different temperatures. As the temperature rises, the degree of reduction of iron oxides and hence the consumption of hydrogen increases from 31.61% at 600°C. to 45.3% at 700°C. and 53.08% at 800°C. The degree of conversion of hydrogen in the reconversion reaction at these temperatures is approximately the same and amounts to 8.85-11.0%. In the next 11 min at 600°C., there is an equal development of the reaction of reduction of iron oxides by hydrogen, characterized by a hydrogen consumption of 12.24%, and reactions of reconversion of carbon dioxide by hydrogen, with a hydrogen consumption of 11.09%.

As the temperature is raised to 700°C., during 11 min of the process, the reaction of carbon dioxide with hydrogen, characterized by a hydrogen conversion of 18.68%, predominates. There are also reductive reactions of iron oxides with hydrogen, with a degree of conversion of 7.88%. At 800°C., during the same period of time, 19.05% of hydrogen is consumed in the main reaction, and 12.38% in the reduction. This shows that a temperature rise promotes the development of the reaction of carbon monoxide reconversion. At 600, 700 and 800°C. during 33 min, hydrogen continues to be predominantly consumed (18.89%) in the reaction with carbon dioxide, and an increase in the degree of consumption of hydrogen in reductive reactions with iron oxides is observed (up to 8.75%).

Analysis of the solid residue after the removal of hydrogen sulfide from the gas at 700-800°C. showed that it contains a substantial amount of pyrophoric iron, which ignites spontaneously in air. The increase in the reducibility of the solid reactant may substantially affect the increase in the degree of hydrogen sulfide removal from gases, maintaining it for a longer period of time than in the case of the experiments described, which lasted 1 hr. Obviously, this will make it possible to increase the degree of consumption of the solid absorbent in the course of removal of hydrogen sulfide from the gases.

The apparent activation energy of the reaction of hydrogen sulfide with iron oxides was determined for the diffusion regime of reaction, and its value for a time of 20 and 40 min from the start of the experiment was 1800 cal/mole.

Table 20.

Effect of Temperature on the Reaction of Hydrogen Sulfide (0.35%) with Hematite (v = 3.5 m/sec; 0.5–1.0 mm Fraction; τ = 0.015 sec).

Time, min	T°, K	1000/T	$W, \frac{g}{\min \times g} \cdot 10^{3}$	Reduced rate $W \times 10^{4}$	log W.
3	773	1,29	8,91	1,563	—3,8068
	728	1,37	6,08	0,889	—4,0511
	673	1,51	4,22	0,558	—4,2530
	623	1,61	2,55	0,3258	—4,4870
10	773	1,29	4,24	0,5255	—4,2799
	728	1,37	2,70	0,3126	—4,5050
	673	1,51	1,99	0,2220	—4,6540
	623	1,61	1,13	0,1203	—4,9289
15	773	1,29	2,78	0,3170	—4,4990
	728	1,37	2,33	0,2607	—4,5839
	673	1,51	1,57	0,1711	—4,7667
	623	1,61	0,52	0,0525	—5,2767

Table 21.

Reaction of Hydrogen Sulfide with Hematite at Different Temperatures (v = 0.69 m/sec; 0.5–1 mm Fraction; τ = 0.15 sec).

Time, min	$T = 500°$ C		$T = 700°$ C		$T = 600°$ C	
	Degree of conversion of H_2S, %	$W, \frac{g}{\min \times g} \cdot 10^{-3}$	Degree of conversion of H_2S, %	$W, \frac{g}{\min \times g} \cdot 10^{-3}$	Degree of conversion of H_2S, %	$W, \frac{g}{\min \times g} \cdot 10^{3}$
10	97,15	0,67	—	—	93,48	0,83
20	96,64	0,63	93,84	0,83	94,50	0,86
30	96,84	0,71	—	—	—	—
40	96,94	0,69	96,52	0,90	95,79	0,90
50	97,10	0,74	—	—	—	—
60	—	—	97,07	0,96	96,08	0,88

Table 22.

Change in Gas Composition during the Reaction of KMA Hematite with Hydrogen Sulfide at Different Temperatures ($v = 0.69$ m/sec; $T = 0.15$ sec).

Temperature, °C.	Reaction time, min	Final gas, vol. %				H_2 for reconversion, %	H_2 for reduction, %
		CO_2	CO	H_2	N_2		
600	3,33	4,09	1,82	11,35	82,74	9,54	31,61
	11,25	3,86	2,13	14,78	79,23	11,00	12,24
	33,33	5,04	0,21	18,38	76,37	1,08	3,65
700	3,80	4,16	2,24	8,31	85,29	11,59	45,38
	11,50	2,51	3,62	14,16	79,71	18,68	7,88
	33,50	2,52	3,63	16,15	77,70	18,79	2,47
800	4,33	4,45	1,70	7,35	86,50	8,85	53,08
	11,75	2,12	3,66	13,22	81,00	19,05	12,38
	33,00	2,43	3,65	13,93	79,99	18,89	8,75

Note. Composition of initial gas (in %): H_2S - 0.33 (at 600°), 0.34 (at 700°) and 0.35 (at 800°); CO_2 - 5.83; H_2 - 19.29, N_2 74.55 (at 600°), 74.54 (at 700°) and 74.53 (at 800°).

Results of experiments on the reaction of hydrogen sulfide with KMA hematite showed that the removal of hydrogen sulfide from the gas can be carried out at 500-800°C. with a sufficient degree of recovery of hydrogen sulfide, amounting to 96-97% during a long period of the reaction.

The experiments also established that when hydrogen sulfide of the gas containing it reacts with hematite at a linear velocity of 0.53 m/sec and a contact time of 0.19 sec, a change in particle size from 0.25-0.5 to 2-3 mm had no appreciable effect on the indices of hydrogen sulfide recovery. This is explained by the fact that under the given experimental conditions there was a large excess of the reactant that provided for a sufficient reactive surface during the entire course of the reaction.

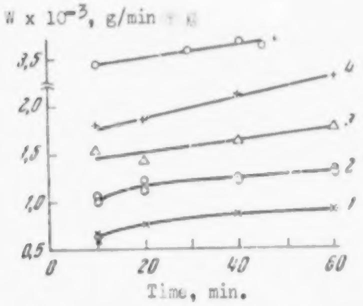


Fig. 28. Change in the rate of the reaction between hydrogen sulfide and hematite with time at different gas feed velocities at 700°C.

$1 - v_1 = 0{,}53$ m/sec, $\tau_1 = 0{,}19$ sec; $2 - v_2 = 0{,}80$ m/sec, $\tau_2 = 0{,}13$ sec; $3 - v_3 = 1{,}04$ m/sec, $\tau_3 = 0{,}096$ sec; $4 - v_4 = 1{,}29$ m/sec, $\tau_4 = 0{,}076$ sec; $5 - v_5 = 1{,}81$ m/sec, $\tau_5 = 0{,}055$ sec.

A large group of experiments were conducted on the removal of hydrogen sulfide from gases with hematite at elevated temperatures. At high gas feed velocities, the linear velocities of the gas supplied ranged from 0.27 to 0.66 m/sec at a hydrogen sulfide concentration in the gas of 0.24% and at linear velocities from 0.53 to 1.81 m/sec, at a hydrogen sulfide concentration of 0.4% (CO_2 8.5%, H_2 18.2%, N_2 72.9%) at 700°C. and a particle size of 0.5-1.0 mm.

As the blast velocity rose from 0.27 to 0.66 m/sec, the rate of the reaction of hydrogen sulfide with hematite increased. The degree of hydrogen sulfide removal from the gas under the indicated conditions was 95-98% during the entire reaction cycle (1hr). A further increase of the feed velocity of the gas being purified led to a substantial increase of the reaction rate (Fig. 28). Under the conditions of the experiments, it was impossible to raise the blast velocity further in order to exclude the diffusion inhibition at 700°C. On the one hand, this was due to the rather high reaction rate at this temperature (a high degree of recovery of H_2S), and on the other, to the large height of the solid reactant (100 mm), which at high blast velocities caused a compaction of hematite and the creation of a large resistance of the layer. Thus one can expect that at 700°C., the rate of this reaction can be higher if a kinetic reaction regime is provided for, i. e., if there are no diffusional inhibitions. Moreover, the experimentally established rate of the reaction of hydrogen sulfide with hematite is acceptable for setting up a technological process of hydrogen sulfide removal from gases at all the blast velocities studied. This is confirmed by the data of Fig. 29, when the degree of hydrogen sulfide conversion at blast velocities of 0.53-1.04 m/sec amounts to 91-94% during 29 min of the reaction, then increases to 94-96% in the course of 40-60 min. For a blast velocity of 1.81 m/sec the degree of purification reaches 99% during 10 min, 96.88% during 29 min, then drops to 77.83% in the course of 45 min. As was already noted in an evaluation of other experiments, a certain decrease of the degree of conversion of hydrogen sulfide during the initial period of the reaction at gas feed velocities of 0.53-1.29 m/sec is due to the reduction of higher iron oxides to lower oxides and iron. Subsequently, the rate of the main process of hydrogen sulfide removal from the gas increases. This is confirmed by data indicating a change in gas composition during the removal of hydrogen sulfide, listed in Table 23.

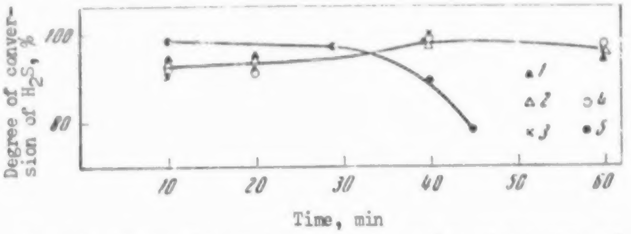


Fig. 29. Change in the degree of conversion of hydrogen sulfide during its reaction with hematite at different gas feed velocities (T = 700°C.; H_2S concentration, 0.4%).

1 - 1.24 m/sec; 2 - 1.04; 3 - 0.83; 4 - 0.53; 5 - 1.81.

During the initial period of removal of H_2S from the gas, i. e., 10 min after the start of the experiment, at a gas feed velocity of 0.27 m/sec, the hydrogen concumption in the reduction processes was 27.9%, and in the reaction of carbon dioxide with hydrogen, 18.1%. During the following period from 30 to 70 min, the predominant role was played by the reconversion reaction, with a hydrogen consumption of 24%, and in the reduction of iron oxides, with 3.55%.

At a blast velocity of 0.52 m/sec after 17-27 min from the start of the experiment, the reconversion $CO_2 + H_2$ predominates, with a hydrogen consumption of 23.8 and 29%; in the reduction of iron oxides, 5.95-4.07% of hydrogen is consumed. At the end of the cycle, after 57 min, only the reaction of carbon dioxide with hydrogen, with a hydrogen consumption of 18.6 and 24.5%, takes place. In a reducing medium, no appreciable evolution of elemental sulfur was observed.

Table 23.

Change of the Gas During the Reaction of KMA Hematite with Hydrogen Sulfide at Different Blast Velocities (t = 700°C., 0.5-1 mm Fraction)

Contact time, sec	Linear velocity, m/sec	Reaction time, min	Final gas, vol. %				H_2 for reconversion, %	H_2 for reduction, %
			CO_2	CO	H_2	N_2		
0,28	0,27	10	5,07	3,35	10	81,58	18,1	27,9
		31	4,0	4,45	13,49	78,06	24,0	3,24
		70	4,0	4,45	13,55	78,00	24,0	3,55
0,20	0,52	27	3,2	4,4	13,0	79,4	23,8	5,95
		57	4,0	4,5	14,83	76,67	18,6	—
0,15	0,65	17	3,0	5,4	12,47	79,13	29,0	4,07
		54	3,9	4,55	14,95	76,6	24,5	—

Note. Composition of initial gas (in %): H_2S 0.24; CO_2 8.5; H_2 18.5; N_2 72.76.

Analysis of the solid residue showed that when hydrogne sulfide reacts with hematite, all of the sulfur passes into iron sulfide. The sulfur content of solid residue in the reaction of hydrogen sulfide with hematite at different gas feed velocities (t = 700°C.) is as follows:

Conditions of gas supply	S_{tot}	S_{sulf}
$v_1 = 0,53$ m/sec $\tau_1 = 0,19$ sec.	9,21	9,12
$v_2 = 0,83$ m/sec $\tau_2 = 0,13$ sec.	13,81	13,64
$v_3 = 1,04$ m/sec $\tau_3 = 0,096$ sec.	16,08	16,0
$v_4 = 1,29$ m/sec $\tau_4 = 0,078$ sec.	17,37	17,0
$v_5 = 1,81$ m/sec $\tau_5 = 0,055$ sec.	16,52	16,18

From the above data it is evident that the total sulfur content of the solid phase corresponds to that of iron sulfide. As the blast velocity increases from 0.53 to 1.29 m/sec, the total sulfur content in the solid reactant rises from 9.21 to 17.37%. At a blast velocity of 1.81 m/sec, it amounts to 16.52% during a shorter reaction period, 45 min. The degree of consumption of the purification reactant rises from 23 to 43.4% as the feed velocity of the gas flow increases from 0.53 to 16.29 m/sec.

The indicated degree of consumption of the absorbent at all the blast velocities studied is sufficient reason for setting up the process of hydrogen sulfide removal from gases.

Thus, the study of the kinetics of the reaction between hydrogen sulfide and iron oxides showed the practical feasibility of the process of hydrogen sulfide removal from gases at 600-800°C. with a sufficient degree of recovery amounting to 95-97% in the course of an hour.

In organizing a complete technological process of removal of sulf compounds from gases, in addition to increasing the economy, it is necessary to plan the conditions of regeneration of the spent reactant and utilization of the recovered sulfur.

As was shown by chemical analysis of the solid residue, all of the sulfur passes from the gas into iron sulfide. The latter can be regenerated by roasting in atmospheric oxygen or by steam-air treatment in which mostly sulfur dioxide is obtained in the gaseous phase and iron oxides in the solid phase.

Studies of the roasting of iron sulfide in atmospheric oxygen were conducted at initial layer temperatures of 600 and 700°C. and a linear air velocity of 0.060 m/sec (contact time about 1 sec). Natural iron sulfide with a sulfur content of 22.18% was subjected to roasting.

Table 24

Roasting of Ferrous Sulfide in Atmospheric Oxygen at Different Temperatures
(v = 0.060 m/sec; τ = 1.0 sec)

Time, min	SO_2, %	Degree of Conversion of S, %	Excess Air α	Time, min	SO_2, %	Degree of Conversion of S, %	Excess Air α
$T = 600°$ C				$T = 700°$ C			
11,50	4,26	4,25	2,71	10,50	4,21	4,85	2,84
17,00	9,06	9,12	1,22	14,00	11,95	9,58	1,00
22,00	8,25	13,50	1,32	17,50	12,97	14,30	1,08
30,00	5,56	18,70	2,20	21,25	13,67	19,30	1,02
45,00	3,47	24,40	3,47	24,66	13,42	24,10	1,04
60,00	1,60	27,30	7,13	28,00	13,97	28,70	1,00

It is evident from the data of Table 24 that at 600°C., an average of 3.5-9% of sulfur dioxide is evolved into the gaseous phase, and the degree of expulsion of sulfur amounts to 27.3% during 1 hour. When the temperature is raised to 700°C., the process of reaction of ferrous sulfide with atmospheric oxygen is accelerated. The amount of sulfur dioxide evolved reaches 11-12% in the gas, and the degree of expulsion of sulfur increases to 28.7% after only 28 min.

A major disadvantage of the process of roasting of ferrous sulfide with air under the indicated conditions is a considerable temperature rise in the layer because of the exothermic character of the reactions taking place; this led to sintering of the charge along the layer and consequently to a decrease in the sulfur expulsion rate.

The process of roasting of ferrous sulfide in the solid phase results primarily in the formation of iron oxides, this being in accord with the analyses of the composition of the solid phase conducted by G. S. Frents [22], who studied the oxidation of iron sulfide by atmospheric oxygen at 600, 700 and 800°C. The main product of the reaction in the residue were iron oxides and also traces of iron sulfate; at 800°C., an appreciable amount of metallic iron is observed.

Possible overheating of the solid absorbent can be minimized by regeneration with steam-air treatment. Studies of the reaction of ferrous sulfide with a steam-air mixture were conducted on the apparatus described earlier, where additional consideration was given to the saturation of air with water vapor until a certain content was reached before the air entered the reactor.

The studies were conducted with a blast in which the ratio of steam to oxygen was 2, 4 and 40 at 600-800°C. The linear velocity of the steam-air mixture was 0.1 m/sec ($\tau = 0.61$ sec) and 0.42 m/sec ($\tau = 0.14$ sec).

It is evident from Table 25 that for a ratio $H_2O/O_2 = 2$ at 600°C., the process practically does not occur. Raising the temperature to 700°C. leads to a considerable increase of the roasting of ferrous sulfide, with the evolution of 13% of sulfur dioxide and traces of hydrogen sulfide into the gaseous phase. The degree of expulsion of sulfur is 44% during 33 min.

A vigorous development of the process of roasting of ferrous sulfide also continues to be observed at 800°C. with the same degree of expulsion of sulfur. However, the distribution of the gaseous products of roasting is somewhat different -- the content of sulfur dioxide is 11-12% and that of hydrogen sulfide, up to 2%.

The steam-air treatment of ferrous sulfide makes it possible to conduct the regeneration process under milder temperature conditions without any appreciable fusion of the charge.

Table 25

Reaction of Steam-Air Mixture with Ferrous Sulfide at $H_2O/O_2 = 2$ ($v = 0.1$ m/sec; $\tau = 0.61-0.64$ sec)

Time, min	H_2S, %	SO_2, %	Degree of Conversion of S, %
$T = 600°$ C			
17	—	0,27	0,63
30	—	1,46	3,35
$T = 700°$ C			
8,50	—	6,01	5,92
12,00	0,109	12,89	11,18
15,16	—	14,33	16,26
18,67	—	13,00	21,34
22,25	0,071	13,56	27,13
26,16	—	13,40	33,56
29,50	0,310	13,36	38,82
33,00	0,100	13,37	44,66
$T = 800°$ C			
10,00	0,467	3,92	7,86
13,50	1,790	11,18	13,07
17,33	1,620	11,18	18,51
20,41	1,800	12,05	23,23
23,58	1,920	11,94	28,40
26,83	1,810	11,52	33,15
29,91	2,070	12,32	37,80
33,00	1,110	12,23	42,35

To increase the hydrogen sulfide content of the final reaction products, the experiments were conducted in the presence of a higher content of water vapor in the blast, $H_2O/O_2 = 4$ at 600, 650 and 700°C.

Table 26

Reaction of Steam-Air Mixture with Ferrous Sulfide at $H_2O/O_2 = 4$ ($v = 0.11-0.12$ m/sec; $\tau = 0.48-0.54$ sec)

Time, min	H_2S, %	SO_2, %	Degree of Conversion of S, %
$T = 600°$ C			
14,66	0,21	2,830	4,86
22,25	0,0068	1,430	6,27
31,00	—	0,999	7,33
$T = 650°$ C			
12,75	0,45	3,06	6,10
17,00	1,80	7,64	10,03
21,50	2,56	7,37	14,10
26,00	2,14	6,91	18,50
31,61	1,96	5,91	23,70
39,00	1,37	4,95	28,80
49,00	1,12	3,65	37,60
57,00	0,82	2,20	40,50
$T = 700°$ C			
11,00	0,44	4,04	5,08
15,08	1,46	10,13	9,19
18,25	2,00	10,79	13,12
21,58	1,56	11,28	17,36
25,00	1,71	11,65	21,75
28,58	3,41	11,29	25,70
32,25	1,71	11,39	30,44
37,00	1,58	9,61	41,82

It is evident from Table 26 that at 600°C., the process of steam-air roasting takes place inefficiently. Raising the temperature to 650°C. causes a considerable increase in the rate of the reaction of the steam-air blast with ferrous sulfide with the evolution of 3 to 7.64% sulfur dioxide and noticeable amounts of hydrogen sulfide, from 1 to 2.5%, into the gaseous reaction products. The regeneration process takes place more intensively at 700°C., when an average of 10-11% sulfur dioxide and 1.5-2.0% hydrogen sulfide are observed in the gaseous phase. The degree of expulsion of sulfur from the solid residue reaches 42%.

A tenfold increase in the steam content of the blast during the steam-air treatment of ferrous sulfide did not result in any appreciable increase in the hydrogen sulfide content of the end products of the reaction at 700-800°C.; on the contrary, it led to a decrease in the expulsion of sulfur to 27-36% in the course of 55 min of the reaction (Table 27).

Table 27

Reaction of Steam-Air Mixture with Ferrous Sulfide at $H_2O/O_2 = 40$
(v = 0.38-0.47 m/sec; T = 0.126-0.156 sec)

Time, min	H_2S, %	SO_2, %	Degree of Conversion of S, %	Time, min	H_2S, %	SO_2, %	Degree of Conversion of S, %
$T = 700°$ C				$T = 800°$ C			
7,00	1,180	3,00	1,24	8,00	1,975	2,30	2,54
10,33	0,490	7,98	5,96	14,00	3,960	2,04	5,43
15,58	0,315	5,04	8,18	20,00	1,350	9,55	12,66
23,00	0,344	4,05	10,08	25,33	1,770	9,72	16,19
27,00	2,420	6,26	12,83	31,58	1,665	9,70	20,18
34,50	2,400	8,52	17,32	37,66	0,012	12,48	24,53
39,00	0,320	9,56	19,67	43,83	0,012	13,07	28,56
43,25	0,600	11,95	21,93	50,50	0,011	12,54	32,40
47,75	0,567	8,26	24,00	56,00	0,172	11,60	36,30
54,25	0,335	6,14	26,66				

The above experiments graphically confirm the conclusions drawn from thermodynamic analysis to the effect that in the overall process of steam-air roasting, the gaseous phase chiefly contains sulfur dioxide and minimum amounts of hydrogen sulfide and elemental sulfur.

The completed study of the regeneration of the solid reactant shows that a practically feasible process consists of steam-air treatment of ferrous sulfide at 700-800°C. with a steam-to-oxygen ratio equal to 2, sulfur dioxide being chiefly obtained in the gaseous phase.

HYDROGEN SULFIDE REMOVAL FROM GASES BY MEANS OF MANGANESE OXIDES

Thermodynamic analysis showed that reactions between hydrogen sulfide and manganese oxides can take place in a reducing medium at 300-900°C. Moreover, the presence of hydrogen and carbon monoxide in the gas undergoing purification may lead to the development of secondary reductive reactions associated with crystallochemical transformations of higher manganese oxides into lower ones.

We studied the reaction of natural manganese ores with hydrogen sulfide by using the procedure described earlier. Hydrogen sulfide was removed from the gases by using an enriched manganese concentrate of grade I of the Nikopol' deposit of the following composition (in %): Mn 44.7; MnO_2 50.5; SiO_2 16.1; Al_2O_3 1.8; Fe_2O_3 2.1; CaO 1.5; MgO 1.0; Na_2O 0.44; S 0.02; K_2O 1.19; P 0.22; CO_2 1.21. The hydrogen sulfide content of the gas being purified was 0.24%, CO_2 6.08%, H_2 18.0% and N_2 75.68%. The linear velocity of the gas supplied was varied from 0.435 to 3.81 m/sec.

The effect of the blast velocity on the degree of conversion of hydrogen sulfide with manganese concentrate is shown in Table 28. As the blast velocity rises from 0.435 to 3.81 m/sec, the degree of conversion of H_2S falls off.

Starting with a gas feed velocity of 3.15 to 3.81 m/sec, the reaction rate becomes independent of the blast velocity during the first 3 min of the reaction. At the indicated gas feed velocities, the diffusional inhibition of the supply of the reactants to the surface where the reaction occurs has little effect.

The effect of temperature on the rate of the reaction of hydrogen sulfide with manganese concentrate was studied at a linear gas velocity of 3.07 m/sec and a contact time of 0.013 sec. The temperature in the layer was maintained at 350, 400 and 500°C. The gas being purified contained (in vol. %) H_2S 0.38; CO_2 5.9; H_2 19.05; N_2 74.67.

The degree of conversion of hydrogen sulfide reached its highest value at 350-500°C. during the first 3 min of the reaction (Fig. 30 a). This figure shows the presence of a minimum degree of conversion of hydrogen sulfide. At 400-500°C. it is observed after 10 min of the reaction, and at 350°C., after 6 min. A similar minimum is noted also in the rate of the reactions of hydrogen sulfide with manganese oxides (Fig. 30 b).

This type of change in the reaction rate of hydrogen sulfide for manganese concentrate may be due to the occurrence of reactions involving the reduction of higher manganese oxides by hydrogen at all the temperatures studied. This is illustrated in Fig. 31, the data of which were used to determine the value

Table 28

Effect of Linear Velocity of the Gas Flow on the Rate of the Reaction of Hydrogen Sulfide with Manganese Concentrate of Grade I of the Nikopol' Deposit

Time, min	Degree of Conversion of H_2S, %	$W, \frac{g}{min \times g} \times 10^3$
$v = 0,435$ m/sec $\tau = 0,092$ sec		
10	97,11	0,94
20	93,95	0,97
30	95,48	1,14
$v = 2,59$ m/sec $\tau = 0,015$ sec		
5	92,08	6,24
10	71,78	5,16
15	40,23	3,13
18	32,36	2,25
$v = 3,10$ m/sec $\tau = 0,0129$ sec		
3	95,16	8,10
6	76,58	5,96
10	59,25	4,70
15	40,63	3,43
$v = 3,74$ m/sec $\tau = 0,0107$ sec		
3	87,90	7,99
6	57,72	5,50
10	39,91	4,05
15	22,19	2,32
$v = 1,92$ m/sec $\tau = 0,021$ sec		
5	95,15	4,60
10	84,09	4,35
15	68,53	3,78
20	49,78	2,77
$v = 2,15$ m/sec $\tau = 0,0127$ sec		
3	93,69	7,50
6	73,97	6,44
10	58,08	5,32
15	41,78	3,98
$v = 3,81$ m/sec; $\tau = 0,0105$ sec		
3	89,11	8,10
6	60,69	5,96
10	40,94	4,34
15	29,44	3,12

of the apparent activation energy for different periods of the reaction - 3, 10 and 15 min.

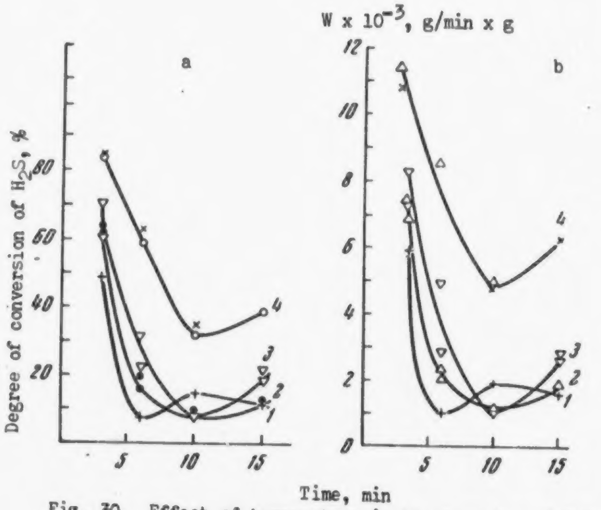


Fig. 30. Effect of temperature in the reaction of H_2S with manganese concentrate of Grade I of the Nikopol' deposit on the degree of conversion (a) and reaction rate (b) (v = 3 m/sec, τ = 0.013 sec).
1 - 350°C.; 2 - 400°C.; 3 - 450°C.; 4 - 500°C.

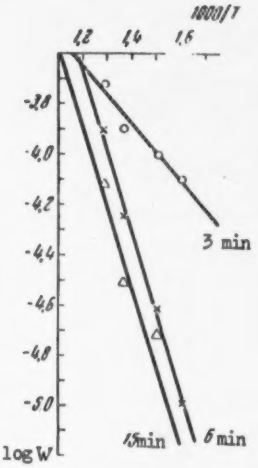


Fig. 31. Logarithm of the rate of the reaction of H_2S with manganese concentrate of Grade I of the Nikopol' deposit versus reciprocal temperature. v = 3.0 m/sec, τ = 0.013 sec

For a reaction time of 3 min, the apparent activation energy was 5078 cal/mole. The reaction value obtained is similar to the value of the apparent activation energy for reactions of reduction of manganese oxides by hydrogen. In the reduction of the manganese mass with a nitric acid mixture at temperatures up to 75-400°C., the activation energy is 6400 cal/mole.

As the reaction time increases from 6 to 15 min, an increase in the apparent activation energy to 14960 cal/mole takes place. Such a value of the apparent activation energy characterizes the process of hydrogen sulfide removal from the gases by manganese concentrate of grade I of the Nikopol' deposit under conditions close to the extrakinetic region.

To purify the gases with a high degree of removal of hydrogen sulfide in the course of a long period of time, the experiments were carried out at elevated temperatures and with an increased contact time on the same reactant.

Table 29 gives the results of experimental data on the effect of temperature from 500 to 800°C. on the removal of hydrogen sulfide from the gas by manganese concentrate at a feed velocity of 0.65 m/sec and a contact time of 0.15 sec.

Table 29

Reaction of Hydrogen Sulfide with Manganese Ore at Different Temperatures (v = -.65 m/sec; τ = 0.15 sec)

Time, min	Degree of Conversion of H_2S, %	$W, \frac{g}{g \times min} \times 10^3$	Degree of Conversion of H_2S, %	$W, \frac{g}{g \times min} \times 10^3$
	$T = 500°$ C		$T = 600°$ C	
10	97,50	5,40	98,50	5,68
30	98,53	6,30	98,00	6,34
50	98,24	6,50	99,20	6,55
	$T = 700°$ C		$T = 800°$ C	
10	97,7	5,53	99,03	5,80
30	98,6	6,42	99,27	6,35
50	98,5	6,58	98,81	6,60

At all temperatures from 500 to 800°C., the rate and degree of purification of the gas were sufficiently high. The degree of purification of the gas amounted to 97-99% in the course of 50 min. During the first 10 min of the reaction at 500-700°C., the purification was 97.5%, and subsequently increased to 98-99%. A certain decrease in the degree of purification during the initial period of the reaction was due to reactions of reduction of manganese oxides by hydrogen. This is confirmed by data on the change of the gas composition presented in Table 30. During the first 3-4 min of purification, the manganese oxides are reduced by hydrogen, and the latter is almost absent in the outgoing gas. In the course of further removal of hydrogen sulfide from the gas, carbon monoxide appears, indicating the presence of reactions of reconversion of carbon dioxide with hydrogen and formation of carbon monoxide, $CO_2 + H_2 = CO + H_2O$.

Table 30

Change in Gas Composition During the Reaction of Manganese Ore with Hydrogen Sulfide at Different Temperatures (v = 0.65 m/sec; T = 0.15 sec)

Temperature, °C	Reaction Time, min	Final gas, vol. %				H_2 For Reconversion, %	H_2 For Reduction, %
		CO_2	CO	H_2	N_2		
500	3,50	2,30	--	1,01	96,69	5,24	90,4
	12,33	0,89	0,55	6,25	92,31	5,24	35,1
	32,50	1,29	0,60	6,41	91,70	5,68	33,4
600	3,28	2,30	—	0,91	96,79	—	91,4
	13,08	1,94	0,82	7,82	89,42	7,82	17,7
	20,33	0,47	0,95	6,40	92,18	9,05	33,2
700	3,45	2,32	—	—	97,68	—	100,0
	11,66	1,19	0,90	4,55	93,36	8,57	48,2
	31,50	0,95	2,43	5,86	90,76	23,20	21,1
800	3,66	2,10	—	—	97,90	—	100,0
	12,50	0,54	0,97	5,87	92,62	9,23	38,1
	31,58	0,32	1,26	6,55	91,87	12,00	25,8

Note. Composition of initial gas (in %): H_2S 0.27; CO_2 2.30; H_2 10.50; N_2 86.93.

In evaluating the degree of consumption of hydrogen in the reaction of reduction of manganese oxides and in the reaction of reconversion of carbon dioxide by hydrogen, it was found that in the first 3-4 min of the process of hydrogen sulfide removal from the gas, approximately 90-91% of the hydrogen is expended in reactions of reduction of manganese oxides, and at 700-800°C., 100% of the hydrogen is consumed in these reactions. Then, during the period from 12 to 33 min since the start of the gas purification process, the reaction of reconversion of carbon dioxide by hydrogen takes place together with the reduction of manganese oxides by hydrogen. As the temperature rises, the consumption of hydrogen in this reaction increases from 5.24 to 12%.

The use of natural manganite showed that it is reactive in the extraction of hydrogen sulfide at 700°C. in the course of 90-120 min, with a degree of purification of 96-100%. This is clearly evident from the data below (v = 0.74 m/sec; $\tau = 0.0965$ sec):

Time, min	31	60	90	120
Degree of Conversion of H_2S, % . . .	99,87	97,64	97,23	96,76
Time, min	9	44	74	90
Degree of Conversion of H_2S, % . . .	100,00	98,84	97,33	96,66

In a tentative evaluation of the effect of pressure on the course of the reaction of hydrogen sulfide with manganite, experiments were carried out at a pressure of 8 g atm at 700°C. with a linear velocity of 2.62 m/sec and a contact time of 0.057 sec. The hydrogen sulfide removal from the gas in the course of 45 min was 100%.

In order to expand the raw material base of the solid reactants for the removal of sulfur from gases and for the use of manganese ores of other deposits, experiments were conducted in which three grades of manganese concentrate of grade II and slime were used.

Sample No. 1 - manganese concentrate of grade II of the Grushevka ore-dressing plant containing 36.1% Mn; 0.28% P. Sample No. 2 - slime obtained from Maksimovska ponds containing (in %): 14.2 Mn; 19.2 MnO_2; 2.6 MnO; 52.8 SiO_2, and 3.3 CaO. Sample No. 3 - manganese concentrate of grade II from the Chkalovsk ore-dressing complex containing 36.3% Mn and 0.203% P.

It is evident from Fig. 32 that the degree of recovery of hydrogen sulfide for samples No. 1 and 3 is approximately the same and amounts to 92-97% in the course of 1 hour. Hence, manganese concentrates of grade II can also be used to remove hydrogen sulfide from gases. As far as manganese slime is concerned, (sample No. 2), a high degree of gas purification is obtained only in the course of 30 min to the extent of 96%, after which an abrupt breakthrough of hydrogen sulfide and a drop of the degree of purification to 21% are observed at a linear gas feed velocity of 1 m/sec and a contact time of 0.1 sec.

A definitive recommendation of the use of manganese slime will require a further study of the physicochemical characteristics of this process of hydrogen sulfide removal from gases.

In view of the fact that sample No. 3 of manganese concentrate of grade II from the Chkalovsk ore-dressing complex was found to be applicable to the extraction of hydrogen sulfide from gaseous mixtures, the subsequent experiments on the effect of temperature were conducted by using this reactant:

	10 min	20 min	40 min	60 min
Degree of conversion of H_2S (%) at temperature (°C)				
600	97,36	95,78	97,83	98,06
700	97,30	96,22	97,46	97,22
800	93,13	95,07	95,81	94,18

From the data cited it is evident that at 600-700°C., a linear gas velocity of 1 m/sec and a contact time of 0.1 sec, manganese concentrate of grade II purifies the hydrogen sulfide containing gas to the extent of 96-97% in the course of 1 hour. At 800°C., during the first 10 min, the hydrogen sulfide removal from the gas is 98%, then decreases to 94.18% after 60 min.

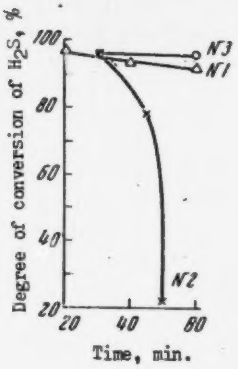


Fig. 32. Change in the degree of conversion of hydrogen sulfide during the reaction with manganese concentrate of grade II (samples No. 1 and 2) and manganese slime (sample No. 3) with time.

In order to set up a complete technological procedure for hydrogen sulfide removal from gases by manganese ore, it is necessary to specify the conditions of regeneration of the spent reactant and of the use of the extracted sulfur.

As was shown by chemical analysis of the solid residue, all of the sulfur from the gas is tied up in manganese sulfide.

The total sulfur content of the reactant was 18-22%, which corresponds to a degree of consumption of the reactant of 25-26%, but this is not the limit, since the degree of purification achieved in the experiments, 95-97% in the course of 1 hour, is still an adequate quantity for subsequent use of the reactant.

The regeneration of manganese sulfide can be carried out by roasting in atmospheric oxygen with the evolution of sulfur dioxide into the gaseous phase and formation of manganese oxides in the solid phase, or by using the steam-air treatment, which also results in the formation of manganese oxides and sulfur dioxide, and partly hydrogen sulfide and gaseous sulfur.

The conditions of roasting of manganese sulfide in atmospheric oxygen were studied by using a chemically pure reactant at 500, 600 and 700°C., at a linear gas feed velocity of 0.061 m/sec and a contact time of 1 sec. The sulfur content of manganese sulfide was 19.7%. Manganese sulfide was first made into pellets, which were then crushed to 0.5-1.0 mm.

The temperature change in the layer resulting from the reaction was recorded by an upper and a lower thermocouple, both of which penetrated the layer to a depth of 5 mm. At an initial temperature of 500°C., the maximum temperature briefly reached 940°C., for t_{in} = 600°C., t_{max} = 960°C., and for t_{in} = 700°C., t_{max} = 1000°C.

A very essential feature was the evolution of sulfur dioxide and of a minimum amount of hydrogen sulfide (up to 1%) into the gaseous phase during the unsteady period of heating to the given temperature of the experiment, and the amount of sulfur dioxide evolved during the heating increased with rising temperature.

Table 31.

Roasting of Manganese Sulfide (MnS) in Atmospheric Oxygen at Different Temperatures (v = 0.061 m/sec; τ = 1 sec)

Time, min	Evolution of SO_2, %	Degree of conversion of S, %	Excess air,	Time, min	Evolution of SO_2, %	Degree of conversion of S, %	Excess air,	Time, min	Evolution of SO_2, %	Degree of conversion of S, %	Excess air,
$T = 500°$ C				$T = 600°$ C				$T = 700°$ C			
Heating.	3,85	6,97	—	Heating.	3,09	7,65	—	Heating.	6,18	21,5	—
4,50	10,35	16,30	3,94	3,66	14,20	18,70	1,00	4,00	9,54	32,8	1,26
7,50	15,19	25,40	1,25	6,66	14,40	27,40	1,00	7,00	13,35	41,0	1,05
10,50	15,12	32,80	1,00	10,25	14,10	37,60	1,00	9,66	13,25	49,0	1,05
13,50	16,63	40,10	1,00	13,66	12,70	46,80	1,10	12,50	13,32	57,2	1,05
17,50	13,02	50,50	1,07	17,00	13,00	56,20	1,07	15,75	14,29	67,2	1,00
21,25	10,80	59,80	1,11	21,00	12,40	66,30	1,12	19,50	12,13	78,0	1,15
				25,00	13,10	77,20	1,02				

It is evident from the data of Table 31 that as the temperature rises, the course of the roasting becomes more vigorous as time goes on. The quantity of sulfur dioxide evolved amounts to an average of 10-15% at all the temperatures studied and over the entire period of the reaction. The optimum roasting temperatures should be regarded as being 600-700°C., when in 20-25 min of the reaction the degree of expulsion of sulfur reaches 77-78%.

Roasting with this amount of sulfur dioxide being evolved into the gaseous phase takes place with an excess air coefficient of 1-1.1. The roasting may occur in such a way that different oxide forms of manganese are formed in the solid phase. It has been established that at 500°C. the oxidation of manganese sulfide involves the formation of manganic oxide (Mn_2O_3) in the solid phase, and at 600 and 700°C., manganous oxide (MnO), provided that sulfur is present in the solid residue.

When the solid absorbent is regenerated by using steam-air treatment of manganese sulfide, depending on the ratio of water vapor and air in the blast mixture, hydrogen sulfide may be obtained in the reaction product in addition to sulfur dioxide.

The steam-air treatment of manganese sulfide was achieved at a linear blast velocity of 0.11 m/sec and a contact time of 0.53-0.58 sec with a steam-to-oxygen ratio of 2 and 4. The sulfur content of the regenerated mass was 19.7%. The temperature varied from 400 to 800°C.

During feeding of the steam-air mixture, the temperature in the layer rose as a result of the exothermic nature of the reaction. Nevertheless, the use of the steam-air blast makes it possible to maintain stable temperature conditions without overheating, thus preserving the original properties of the material being roasted.

The data listed in Table 32 show that at all the temperatures studied, a high degree of desulfurization is observed that during 25 min of the reaction amounts to 80%. The bulk of the sulfur is evolved in the form of sulfur dioxide (content in the gas, 10-14%), and a slight amount of it is converted into hydrogen sulfide (content in the gas up to 2%) and elemental sulfur. The evolution of misty gaseous sulfur that remained practically untrapped was observed visually.

In order to increase the hydrogen sulfide content in the end products obtained, experiments were carried out with a large supply of steam ($H_2O/O_2 = 4$) at 500 and 800°C. However, as is evident from the data of Table 33, no substantial increase of hydrogen sulfide occurred in the gaseous phase, and the degree of expulsion of sulfur, other conditions being equal, underwent little change.

The studies made on the steam-air treatment of manganese sulfide confirmed the conclusions of the thermodynamic analysis that in a gas at equilibrium, for the conditions under consideration, the main substance formed is sulfur dioxide, with smaller amounts of hydrogen sulfide and elemental sulfur.

In evaluating the conditions of roasting of manganese sulfide, of great interest are the studies of V. I. Chagunava [16], who carried out studies on

Table 32.

Reaction of Steam-Air Mixture with Manganese Sulfide at $H_2O/O_2 = 2$ ($v = 0.10–0.11$ m/sec; $\tau = 0.53–0.58$ sec)

Time, min	H_2S, %	SO_2, %	Degree of Conversion of S, %	Time, min	H_2S, %	SO_2, %	Degree of Conversion of S, %	Time, min	H_2S, %	SO_2, %	Degree of Conversion of S, %	Time, min	H_2S, %	SO_2, %	Degree of Conversion of S, %
$T = 400$° C				$T = 500$° C				$T = 600$° C				$T = 800$° C			
5,50	—	9,47	14,57	2,50	0,08	8,82	7,62	4,16	0,74	8,43	10,34	5,42	0,29	8,71	10,96
10,40	0,39	12,01	30,77	5,25	0,57	15,27	18,47	7,08	0,49	13,40	21,01	8,17	1,16	13,09	20,05
14,00	—	12,58	43,31	8,25	0,60	14,38	29,27	10,58	0,61	13,29	33,03	10,59	1,72	14,55	29,10
18,00	—	12,83	56,73	10,50	0,80	12,64	37,78	14,33	1,17	12,51	46,46	12,83	2,02	22,09	38,40
21,67	—	12,64	69,01	14,42	0,55	13,36	52,60	17,16	1,22	12,57	58,61	14,50	1,33	14,40	44,70
25,25	—	13,98	85,94	18,33	0,75	11,66	64,82	20,75	1,06	12,84	70,22	17,00	1,17	13,29	53,80
30,00	—	9,08	97,14	21,42	0,59	12,12	75,18	24,33	0,18	12,40	80,51	21,00	1,24	13,53	66,72
50,00	0,017	12,81	100,00	25,58	0,82	11,14	87,42	28,00	0,62	12,16	90,84	25,00	1,08	12,10	78,50

the desulfurization of benzene involving removal of organic sulfur and hydrogen sulfide by a manganese contact mass (MnO), followed by regeneration of manganese sulfide with a steam-air mixture with different air-to-steam ratios (2:1, 4:1, 7:1) at 600-700°C.

Table 33.

Reaction of Steam-Air Mixture with Manganese Sulfide, $H_2O/O_2 = 4$ ($v = 0.11$ m/sec; $\tau = 0.55$-0.59 sec.

Time, min	H_2S, %	SO_2, %	Degree of Conversion of S, %	Time, min	H_2S, %	SO_2, %	Degree of Conversion of S, %
$T = 500°$ C				$T = 800°$ C			
5,58	—	10,87	10,10	5,50	1,05	8,92	10,7
9,55	—	12,40	18,28	9,08	1,49	10,96	23,2
12,91	0,017	13,71	25,90	12,91	1,29	11,61	32,2
16,58	0,192	12,43	33,19	16,16	1,14	11,95	43,0
20,16	0,081	12,92	42,68	19,88	1,07	11,61	54,3
23,36	0,117	13,25	51,04	22,91	1,43	11,91	62,8
27,33	0,105	12,24	66,58	26,58	1,48	11,74	73,8
31,00	0,0162	13,18	76,02	30,00	1,07	11,57	83,0

At the indicated temperatures, a high degree of desulfurization is achieved (90-99%). The activity of the purifying mass changes slightly after 8 cycles of absorption of sulfur compounds and regeneration. In the solid phase, the crystalline form of the initial substance after the regeneration is preserved. This is confirmed by x-ray structural analysis of the solid phases.

In addition, thermograms of the sulfide mass and of the same mass after regeneration and secondary sulfidization were almost identical. Oxidation of manganous oxide and manganese sulfide by the steam-air mixture takes place partially before the formation of pyrolusite, as indicated by the pyrolusite and β-kurnakite effect at 600-700 and 965-975°C. Endothermic effects of decomposition of manganese sulfate are absent from the diagrams.

In the course of steam-air treatment of manganese sulfide, no appreciable amounts of manganese sulfate can be formed in the roasted mass because of its reduction by the sulfide with the evolution of sulfur dioxide into the gaseous phase. The absence of SO_4 ions from the regeneration products was established by chemical and roentgenometric analyses.

II

REMOVAL OF SULFUR DIOXIDE FROM GASES

Sulfur dioxide, which is present in relatively low concentrations in the waste gases of industrial enterprises, is the chief cause of pollution of the air reservoir. For this reason, the problem of sanitary protection of air purity is primarily one of recovery of sulfur dioxide from the so-called poor sulfur gases discharged into the atmosphere.

This applies primarily to the purification of the flue gases of thermal electric power plants operating on sulfur-containing types of fuel (mazuts, coal) containing 0.3-0.6% sulfur dioxide. The amount of these gases is increasing enormously and steadily in connection with the rapid development of thermal-power engineering.

At the present time, a large number of flue-gas purification processes are known which have been the subject of numerous studies, and in many cases, of experimental industrial research, but they do not include methods suitable for industrial application that would permit an economical recovery of sulfur dioxide from these gases. In order to solve this problem, which is of major practical importance, it is necessary to make full use of the results of previous studies.

SURVEY OF PROCESSES AND METHODS OF REMOVAL OF SULFUR DIOXIDE FROM GASES

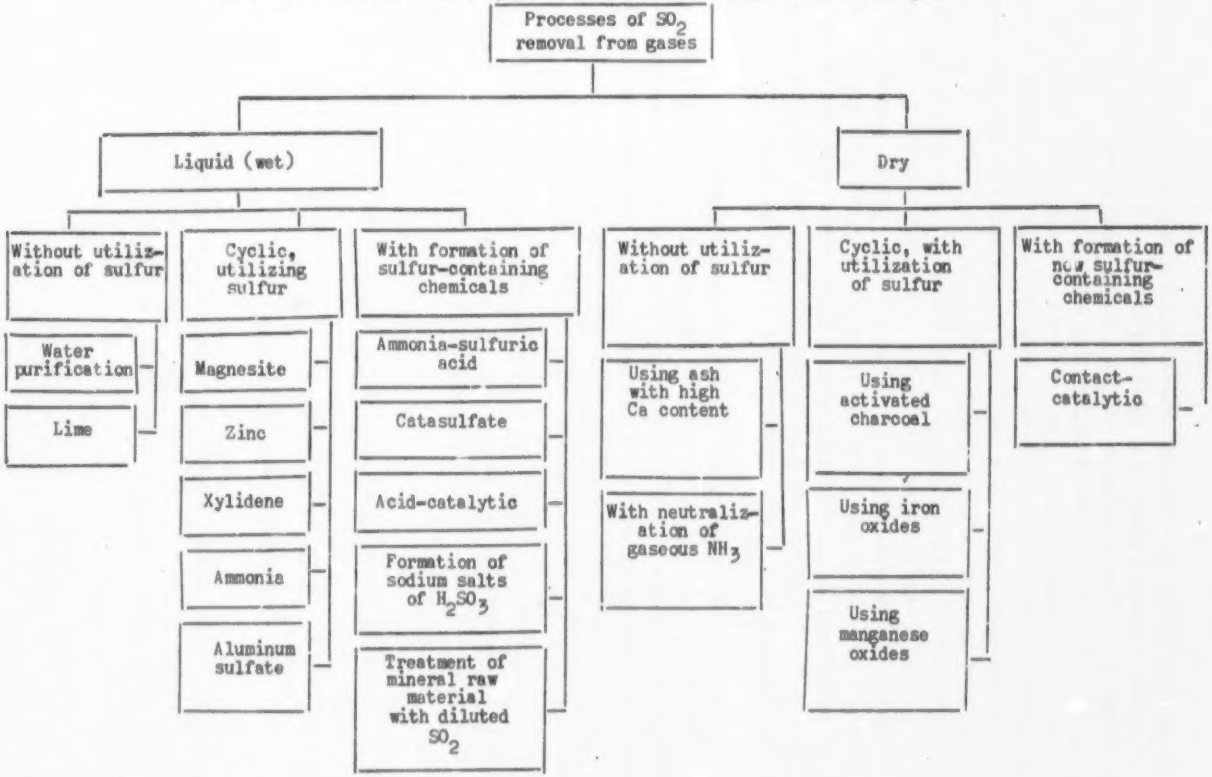
A classification of the processes of sulfur dioxide removal from gases proposed and studied thus far can be arrived at by using the same criteria as in the classification of processes of hydrogen sulfide removal from gases (chart 2).

It is useful first of all to divide all the processes into two main categories differing in the physical state of the main reactant used for recovering sulfur dioxide from gases.

The first category includes processes involving the use of a liquid phase (liquid or "wet" processes) and therefore carried out at relatively low temperatures.

The second category includes processes and methods based on the reaction between the gas and a solid phase (processes of "dry" purification). Here there are no temperature limitations on the main reaction, which is characteristic of processes of "wet" purification related to the evaporation temperature of the liquid phase.

Chart 2. Classification of processes of sulfur dioxide removal from gases.


Processes of SO_2 removal from gases
Liquid (wet)
Dry
Without utilization of sulfur
Water purification
Lime
Cyclic, utilizing sulfur
Magnesite
Zinc
Xylidene
Ammonia
Aluminum sulfate
With formation of sulfur-containing chemicals
Ammonia-sulfuric acid
Catasulfate
Acid-catalytic
Formation of sodium salts of H_2SO_3
Treatment of mineral raw material with diluted SO_2
Without utilization of sulfur
Using ash with high Ca content
With neutralization of gaseous NH_3
Cyclic, with utilization of sulfur
Using activated charcoal
Using iron oxides
Using manganese oxides
With formation of new sulfur-containing chemicals
Contact-catalytic

Each of these categories can in principle be subdivided into three main groups differing in the characteristics of utilization of the sulfur dioxide being recovered.

The first group includes processes whose main purpose is gas purification as such, without considering the possibilities of utilization of the recovered sulfur dioxide. The products of the main reaction of sulfur dioxide with any given reactants constitute the waste in this case and are discarded. This group includes the first attempt to actually achieve sulfur removal from flue gases, i.e., the process of purifying the gases by washing with water. In this process, the bulk of the SO_2 dissolves in the water directly, and a certain amount reacts chemically, in the form of sulfuric acid thus formed, with the salts $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ present in the water to form $CaCO_3$, $MgCO_3$ and carbon dioxide. The main difficulty in removing SO_2 from gases by means of water lies in the large amount of water required (5000-6000 m^3 at 50°C. per ton of recovered sulfur), which after washing of the gas acquires an acid reaction. Moreover, the discharge of the acid water into reservoirs is environmentally just as harmful as the discharge of sulfur dioxide into the atmosphere.

The removal of sulfur dioxide from gases by dissolution in very dilute aqueous solutions of alkaline salts has been carried out in England in installations of the Battersea electric power plants and at Bankside. Here advantage was taken of the high natural alkalinity of the waters of the Thames River and of the possibility of discharging the was waters into it. The degree of removal of SO_2 from the gas was 90-95% [5].

Nor is the sulfur of flue gases utilized in the lime process of purification based on the neutralization of sulfur dioxide with slaked calcium oxide, which is supplied in the form of lime milk or of a suspension of finely divided active limestone.

The process is described by the following equations:

$$SO_2 + H_2O = H_2SO_3,$$
$$Ca(OH)_2 + H_2SO_3 = CaSO_3 + 2\,H_2O.$$

The calcium sulfite obtained is poorly soluble in water (0.138 g/l) and in the course of purification of the gases precipitates out of solution in the form of fine crystals. A side reaction is the oxidation of sulfite to sulfate by oxygen

$$2\,CaSO_3 + O_2 = 2\,CaSO_4.$$

The waste of the process using the lime method is a slime consisting of calcium sulfite and sulfate. It is technically undesirable to subject this slime to regeneration, even though the studies performed established that it can be used in the production of binders, but it has not been used in industry thus far. Under laboratory conditions, the lime process has been tested by the All-Union Heat Engineering Institute im. F. E. Dzerzhinskiy (VTI) and, on a larger scale, in an experimental unit of the Kashira State Regional Electric Power Plant [21]. This process is characterized by a relative simplicity and achieves a practically complete removal of SO_2. However, the substantial consumption of the reactants, coupled with the impossibility of their regeneration and utilization of sulfur and the lack of industrial consumers of the slime, make the lime process uneconomical and unpromising.

The second group includes the so-called cyclic processes and methods, with the formation of commercial sulfur dioxide or elemental sulfur. Here, sulfur dioxide is removed from the gases by means of reactants that are subjected to regeneration and recycled for subsequent reuse.

In dry cyclic processes, which will be discussed in more detail below, sulfur dioxide is absorbed from the gases by activated carbon or other solid reactants.

The absorbents used in liquid cyclic processes are various solutions: ammonia, organic amines (xylidene, pyridine), suspensions of metal oxides (MgO, CaO, ZnO) and others.

Regeneration of the absorbents in these processes is carried out by heating the solution and driving off the SO_2 in a stream of water vapor, or by calcining the filtered sparingly soluble sulfate salts in ovens.

Among the many proposed liquid cyclic processes of extraction of SO_2 from flue gases, the greatest interest among researchers and in industry has been shown in the ammonia, magnesite, zinc and xylidene processes.

The cyclic ammonia process is characterized by the following reactions of formation of ammonium sulfite and bisulfite:

$$SO_2 + 2NH_3 + H_2O \rightleftarrows (NH_4)_2SO_3,$$
$$(NH_4)_2SO_3 + SO_2 + H_2O \rightleftarrows 2NH_4HSO_3.$$

The pressure of SO_2 and NH_3 above the ammonium sulfite and bisulfite solutions may range over considerable limits and depends on the ratio of the concentrations of the neutral and acid salts. This ratio can be chosen so that the partial pressures of SO_2 and NH_3 are negligible. Such a solution can then be used to absorb SO_2 almost without losing any NH_3.

Therefore, in absorbing SO_2 from gaseous mixtures, use is made not of ammonia water alone, but of a solution containing certain proportions of $(NH_4)_2SO_3$ and NH_4HSO_3. The optimum temperature of the purification process is 30°C. The ammonium bisulfite obtained as a result of absorption of SO_2 is an unstable compound undergoing regeneration relatively easily during boiling, with the formation of sulfur dioxide and ammonium sulfite, which can be used again in gas purification.

In the process, ammonium sulfite is partially oxidized by the oxygen usually present in the waste gases to ammonium sulfate, which accumulates in the circulating solution. To extract the sulfate, part of the solution is continually or periodically brought out of the cycle and evaporated, causing separation of sulfate crystals, and the solution is returned to the system. The oxidation of ammonium sulfite can be substantially decreased by adding inhibitors, for example, paraphenylenediamine (0.05-0.1% of the weight of the solution), to the solution. The ammonia method of flue gas purification has been studied in detail in the USSR [24] and the U.S.A. [23].

Operation of an experimental-industrial unit trapping SO_2 by the ammonia method at Thermal Electric Power Plant 12 of the Moscow Regional Administration of the Power Economy showed that the gases emitted into the atmosphere after the purification contained a certain amount of ash, ammonium salts, and a mist, causing undesirable sanitary conditions in the area around the unit. For this reason, the setup also included wet electrostatic precipitators for final purification of the waste gases. The flue gases subjected to purification by the cyclic ammonia method should be first recooled to 30-35°C. In view of the enormous attendant heat loss (the temperature of the flue gases is 120-140°C.), and bulk of the unit, and considering the relatively low indices of the main process, the cyclic ammonia method of SO_2 removal from gases holds little promise for industrial application.

The magnesite cyclic process is based on the absorption of sulfur dioxide by a suspension of magnesium oxide in water. This involves the formation of magnesium sulfite poorly soluble in water, according to the reaction $MgO + SO_2 = MgSO_3$. As it is formed, it precipitates out of the solution in the form of $MgSO_3 \cdot 6H_2O$ crystals. After filtering and dehydration, magnesium sulfite is roasted at 1000°C., and decomposes at this temperature into the component parts $MgSO_3 = MgO + SO_2$. Sulfur dioxide is thus obtained with a concentration sufficient for the production of sulfuric acid (8-10%). Magnesium oxide is reused for the absorption of SO_2.

During the purification of the gases and also during drying and roasting of the sulfite, a certain part of the latter is oxidized to sulfate, which after filtering remains in solution. The recovery from the solution of crystalline magnesium sulfate, which constitutes a commercial product, is carried out by evaporating the solution.

In the USSR, the magnesite method of gas purification was developed by the "Gazoochistka" trust and VTI and was tested on a large pilot unit for purifying the flue gases at the Kashira State Regional Electric Power Plant [21].

The magnesite process is not applicable to the purification of flue gases of electric power plants because of the complexity of the layout, the necessity of a complete removal of ash from the gases, and mainly because of the large heat loss because of the drying and decomposition of magnesium sulfite, which reaches 4% of the amount of fuel consumed by the electric power plant.

Very similar to the magnesite process of removal of sulfur dioxide from flue gases is the cyclic zinc process, based on the production of zinc sulfate and thermal decomposition of the latter into SO_2 and ZnO. The advantage of using zinc oxide over magnesium oxide is the lower dissociation temperature of the acid sulfate salt (260 instead of 650°C.) and the possibility of obtaining sulfur dioxide of high concentration (up to 100%) by this reaction.

However, the difficulties involved in the regeneration of the zinc sulfate which is thus inevitably obtained, the complexity of the technological flow scheme and the high cost of the main reactant, zinc oxide, have been responsible for the lack of development of this process.

Cyclic liquid processes based on the adsorption of sulfur dioxide by aromatic amines, particularly xylidene $C_6H_3(CH_2)_2NH_2$, have also been unsuitable for the recovery of sulfur dioxide from flue gases. The adsorption capacity of xylidene relative to sulfur dioxide is many times that of water, but its use in the pure form is impossible because of the formation of crystalline xylidene sulfate, so that the absorbent usually employed is a mixture of xylidene with an aqueous solution of soda. Xylidene is toxic and possesses a certain volatility, and therefore the waste gases following absorption should be washed with sulfuric acid, which greatly complicates the flow scheme.

The third group of processes of sulfur dioxide removal from gases includes those in which sulfur dioxide is recovered and utilized in the production of new chemicals. This group of processes is characterized by the fact that the absorbent is not recycled into the process, but used in the reaction with sulfur dioxide.

Dry processes of this group include treatment mainly of the mineral raw material (phosphorites, ores, salts, and others) with sulfur dioxide.

Among liquid processes of the third group, the most important are those in which the absorbent used is ammonia, so that the production of ammonia fertilizers can be achieved.

For example, practical applications have been found for the ammonia - sulfuric acid process based on the reaction

$$2NH_4HSO_3 + H_2SO_4 = (NH_4)_2SO_4 + 2SO_2 + 2H_2O.$$

A drawback of this process is a substantial consumption of ammonia and sulfuric acid.

The same group includes the "catasulf" process.

Of practical interest is the process, verified under laboratory conditions [24], of production of sodium sulfates through absorption of SO_2 by solutions of alkalis or carbonates. However, considering the small industrial demand for sodium salts, this process cannot be widely applied in the removal of sulfur from flue gases.

Among other liquid processes of this group we can mention the production of silute sulfuric acid through catalytic oxidation of sulfur dioxide by oxygen in an aqueous medium.

The catalysts used are ions of metals - iron and manganese. This process requires a thorough removal of ash and catalyst-poisoning impurities from the gases, and because of the low rate of the principal reactions and large consumption of the catalyst, it is unsuitable for the purification of flue gases.

Considering the general and comparative evaluation of the proposed processes for removing sulfur dioxide from flue gases, one should note that they do not pertain to processes occurring in boiler units, and for this reason the problems of corrosion of power plant equipment and contamination of the heating surfaces of boilers are not at all solved by using just any methods of sulfur removal. As far as the proposed liquid processes of sulfur removal from flue gases are concerned, they all require deep cooling to 30-40°C, since they are based on the use of aqueous solutions or suspensions of certain reactants. As a result, the buoyancy of the gases discharged from the smokestacks decreases sharply, resulting in a harmful increase of the concentration of carbon dioxide in the ground layers of the air reservoir. Nevertheless, from a technical point of view liquid processes do solve in various degrees the problems of removal of sulfur dioxide from gases. However, on the basis of technical-economic considerations, present-day liquid processes of sulfur removal from flue gases do not meet the requirements of thermal power engineering.

This conclusion has been reached both in the USSR and abroad on the basis of a serious technical-economic study of this problem. Thus, in 1961, the institutes "Giprogazoochistka" and "Giprokhim" carried out a detailed technical-economic study of a few of the most promising processes of purification of flue gases, i.e., the limestone, magnesite, zinc, and ammonia processes. It was shown that the construction of sulfur-removing units at electric power plants is not profitable as compared with the construction of chemical plants of equivalent output, and can be justified only by considerations of preservation of air purity.

Calculations of the overall effect of the use of the indicated liquid processes, carried out in recent years, revealed a 3-4% decrease in the thermal economy of electric power plants as compared with direct combustion and discharge through high smokestacks, and a substantial increase (up to 20%) in the specific capital investments and operational expenditure. Unfavorable technical-economic characteristics of liquid processes of sulfur dioxide removal from flue gases have been responsible for the fact that at the present time, both in the Soviet Union and abroad, further studies and development of these processes have been practically discontinued.

The researchers' attention has switched to the development of dry sulfur removal processes for which some encouraging prospects have been noted in electric power plants. Here the work is developing in two directions: development of processes of dry trapping of sulfur dioxide from the flue gases past the boiler unit and before their entrance into the smokestack, and creation of processes of dry sulfur removal directly in the boiler unit itself.

A characteristic feature of the methods developed is their development chiefly as cyclic adsorption processes. They are based on the absorption of sulfur dioxide by solid adsorbents (activated carbon, silica gel) or reactants (metal oxides) at moderate temperatures, followed by regeneration at higher temperatures by driving off the sulfur dioxide through calcination or blowing hot air or steam.

The absorptive capacity of silica gel (S) and activated carbon (A.c.) for SO_2 was studied by G. I. Chufarov [25] and I. N. Kuz'minykh [26]. The characteristics of these adsorbents are as follows:

	S	S	A.c.	A.c.
SO_2 content of gas, vol. %	2	4	2	4
Absorptive capacity of SO_2 per 100 g of adsorbent, g				
at 0°C	9,5	13,0	19,0	24
at 10°C	8,5	11,0	16,0	20
at 20°C	7,0	8,8	12,5	17

In order to drive SO_2 out of the spent adsorbent, the silica gel must be heated to 130°C., and the activated carbon to 250°C. In the course of removal of SO_2 from the gases by activated carbon in the presence of oxygen and water vapor, coal simultaneously acts as the catalyst in the formation and then adsorption of sulfur trioxide and sulfuric acid.

I. F. Zemskov [27] studied the purification of flue gases by various types of activated carbon. According to the experimental data, the sorption of 1 T of sulfur dioxide requires 5-6 T of activated carbon of type SKTD-1.

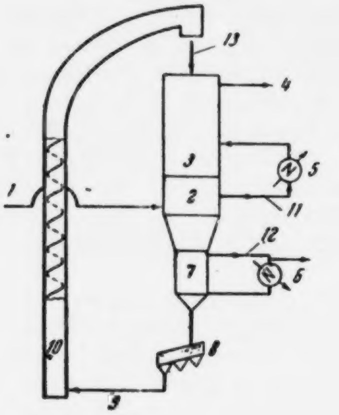


Fig. 33. Technological diagram of assembly for the removal of sulfur dioxide from flue gases by activated carbon at an electric power plant.

1 - flue gas; 2 - first stage of adsorber; 3 - second stage of adsorber; 4 - purified flue gas; 5 - cooler; 6 - heater; 7 - desorber; 8 - screen; 9 - coke; 10 - coke elevator; 11 - purified flue gas; 12 - enriched SO_2 gas; 13 - coke.

The process of sulfur dioxide removal from flue gases by activated carbon is being developed on a large scale in the German Federal Republic at moderate temperatures (up to 50°C) and relatively elevated ones (100-160°C). Experiments on sulfur removal at moderate temperatures showed that the process is difficult to carry out technologically even if one neglects the fact that it produces ash-contaminated sulfuric acid of low concentration (7-15%) [28].

More promising prospects for the use of activated carbon for sulfur removal from flue gases were discovered at temperatures of around 160°C. The sulfur dioxide adsorbed at temperatures above 50°C. can be recovered from the charcoal in the form of sulfuric acid on heating to 250°C. The activated charcoal is regenerated at 350-450°C. without access of oxygen. Such a process, known as the "reinluft" process, was carried out in 1959 on a unit with an output of up to 2000 m^3/hr of flue gases at the Wolfsburg electric power plant (Fig. 33) [29].

In 1967, a report was published [30] to the effect that the process was being carried out on a larger installation (near Dortmund). The adsorbent used in this process may be fine-grained peat semicoke and also semicoke obtainable from brown or bituminous coal. Additional activation of these types of adsorbents is carried out directly in the course of sulfur removal in the presence of SO_2 and of the sulfuric acid obtained.

In addition to processes based on the adsorption of sulfur dioxide, the literature contains material on research on other dry processes of sulfur removal from flue gases, in particular, by means of iron oxides and manganese oxides. Laboratory experiments on the purification of gases using iron oxides [31] showed that at 200-450°C. at a ratio of iron oxides to SO_2 slightly higher than stoichiometric, in the presence of oxygen, sulfur dioxide is oxidized to SO_3. The process of regeneration takes place at about 600°C. Judging from the published information, a more advanced process of sulfur removal from flue gases using manganese oxides was proposed in Japan [32]. The main reactant used here is a powder of activated MnO_2, which spreads throughout the stream. On reacting with MnO_2, sulfur dioxide and trioxide form manganese sulfates, which are recovered together with the unreacted MnO_2 in a cyclone and an electrostatic precipitator. A technological diagram of such a process is illustrated in Fig. 34.

On the basis of the results obtained with an installation operating according to this process, with an output of 3000 m^3/hr of flue gases, a semi-industrial plant with an output of 150,000 m^3/hr is now being constructed at the electric power plant of Iokeiti (Honshu).

Among dry sulfur removal methods, of major interest is a process based on the catalytic oxidation of sulfur dioxide to the trioxide followed by its evolution in the form of sulfuric acid.

Essentially, this process is analogous to that of production of sulfuric acid by the contact method and differs from it in the concentration of sulfur dioxide in the gaseous mixture (0.2-0.4 instead of 7-8%). A technological diagram of an installation utilizing such a process is given in Fig. 35.

A contact-catalytic process of purification of flue gases is being developed with promising results in the German Federal Republic [33] and U.S.A. [37].

Of considerable interest are the possibilities of recovering sulfur dioxide from gases directly in the boiler unit. Research by the Perm Pharmaceutical Institute conducted in collaboration with the Kizel State Regional Electric Power Plant No. 3 in 1961 showed the feasibility of removing sulfur dioxide from the flue gases of a thermal electric power plant by introducing finely crushed limestone into the high-temperature zone of the furnace separately from the sulfur coal [41].

The experiments were carried out by using Kizel coal, the Gubakha intermediate product, and a mixture of coal with the intermediate product. Limestone of the Vsevolodo-Vil'va quarry, containing 85.2% of calcium carbonate, was used as the reactant for the absorption of SO_2. The limestone dust was blown into the 1000-1200°C. zone through eight nozzles located along the front and side walls of the boiler at different angles of inclination. The

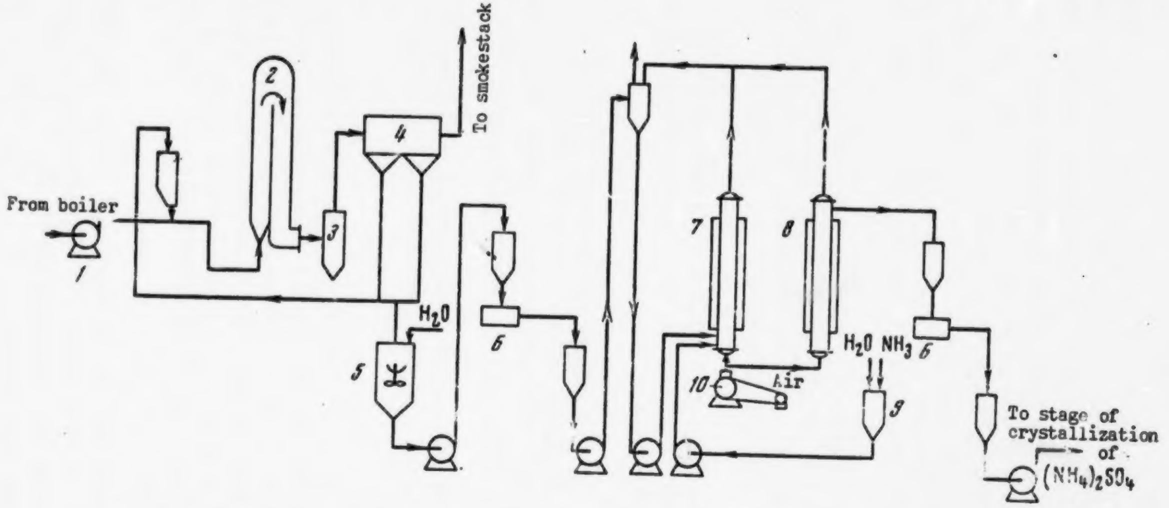

From boiler
1
2
3
4
To smokestack
H$_2$O
5
6
7
8
10
Air
H$_2$O NH$_3$
6
9
To stage of crystallization of (NH$_4$)$_2$SO$_4$

Fig. 34. Technological diagram of the process of flue gas purification by means of manganese dioxide.
1 - flue gas blower; 2 - absorber; 3 - multistage cyclone; 4 - electrostatic precipitator; 5 - dissolver; 6 - filter; 7 - oxidizing column; 8 - stripping column of NH_3; 9 - dissolver of NH_3; 10 - air compressor.

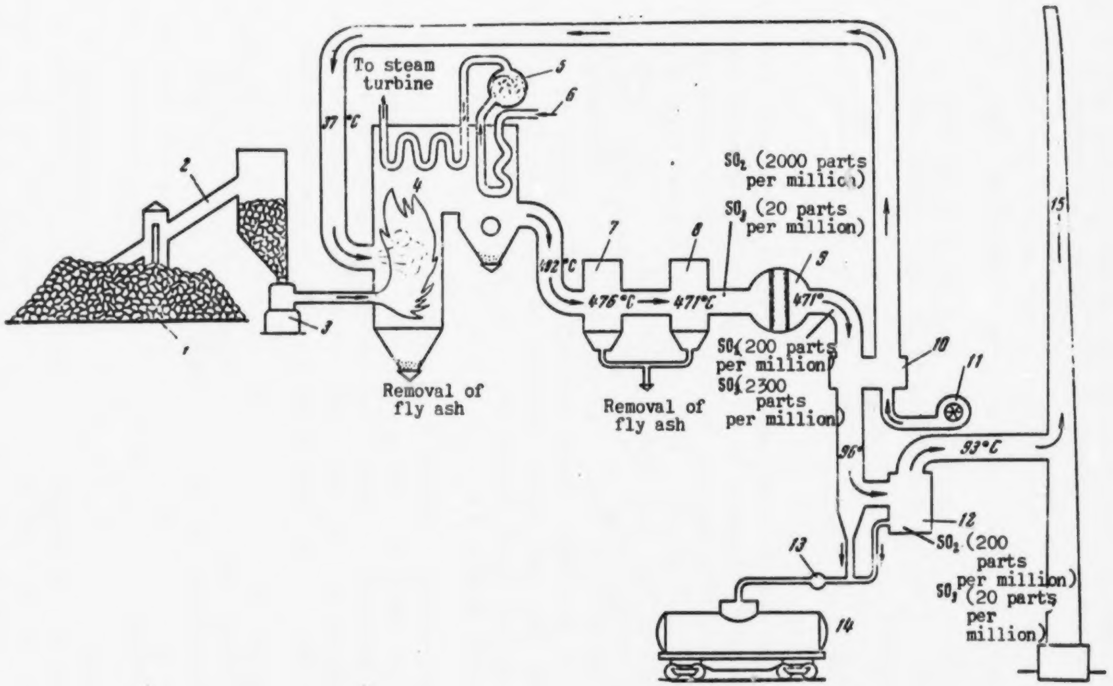

To steam turbine
37 °C
1
2
3
4
5
6
Removal of fly ash
182 °C
7
8
476 °C
471 °C
SO₂ (2000 parts per million)
SO₃ (20 parts per million)
9
471°
SO₂(200 parts per million)
SO₃(2300 parts per million)
Removal of fly ash
10
11
96°
93°C
12
SO₂ (200 parts per million)
SO₃ (20 parts per million)
13
14
15

Fig. 35. Technological diagram of contact catalytic process of sulfur dioxide removal from flue gases.

1 - coal; 2 - coal conveyor; 3 - coal mill; 4 - boiler; 5 - steam collector; 6 - feed water; 7 - mechanical dust collector; 8 - high-temperature electrostatic catcher; 9 - converter; 10 - air heater; 11 - air blower; 12 - electrostatic precipitator for acid; 13 - oxygen pump; 14 - sulfuric acid; 15 - smokestack.

experiments were carried out over the course of nine weeks in order to determine the effect of the amount of limestone supplied to the boiler furnace, of arrangement and angle of inclination of the limestone nozzles, and of working load of the boiler on the degree of purification and temperature of dew point, fuel of different sulfur contents being used.

Given below are experimental data showing the effect of the amount of limestone supplied on the degree of removal of SO_2 from flue gases:

Amount of limestone, % of stoichiometric	0	40	60	80	100	120
SO_2 concentration, %						
coal	0,432	0,333	0,289	0,252	0,193	0,126
industrial product	0,593	0,451	0,403	0,34	0,252	0,163
Degree of purification, %						
coal	—	22,8	31,0	41,5	54,2	70,8
intermediate product	—	24,3	33,1	43,1	57,2	72,6

The industrial tests performed confirmed the fundamental possibility of removing sulfur dioxide from flue gases by limestone injected separately from the fuel. However, even this method is characterized by disadvantages, i.e., a low degree of purification and a high content of limestone dust in the outgoing gas. A similar study was made in the U.S.A. [28], where a study was made of the effect of sulfur removal from gases leaving the furnaces during the combustion of anthracite coal. It was shown that limestone should not be recommended for introduction into the burning coal, since it may react with the silica present in the coal dust. Limestone was found to be more effective than dolomite, and a small amount of iron in the limestone increases the efficiency of the sulfur trapping.

Positive results with sulfur removal from flue gases during blowing of dolomite dust into a boiler furnace were obtained in the German Federal Republic at the Wolfsburg electric power plant, which operates on sulfur mazut [10]. The study showed the optimum particle size of dolomite to be 10-60 μ. The residence time of the flue gases in the boiler was 6 sec.

In addition to the recovery of sulfur compounds directly in the boiler unit by means of some reactants or others introduced from the outside, of scientific and practical interest are the studies of N. G. Titov and L. A. Borozdina, aimed at elucidating the conditions under which the ash of solid fuels may be a necessary reactant in the sulfur removal process [35].

The authors showed that the presence in the coals of minerals that are usually present and whose composition includes calcium and magnesium does not influence the decrease in the content of sulfur compounds in flue gases, since the dissociation of these minerals with the formation of CaO and MgO proceeds at high temperatures, after the bulk of the sulfur gases have been driven out of the furnace. However, in the presence of calcium and magnesium humates in the fuels (lowland peats, some forms of brown coals), the starting combustion stage is accompanied by the decomposition of these humates at temperatures of about 200-300°C., with the appearance of calcium and magnesium oxides capable of binding the sulfur oxides formed into involatile sulfates.

The degree of conversion of sulfur oxides into sulfates depends not only on the quantitative relationships of humates and sulfur in the coal, but also on the mode of combustion of the fuel.

THERMODYNAMICS OF THE REACTIONS BETWEEN SULFUR DIOXIDE AND METAL OXIDES

The process of removal of sulfur dioxide from gases at high temperatures, like the high-temperature recovery of hydrogen sulfide from gases, is best accomplished technically by using solid reactants that are stable at these temperatures and after reacting with SO_2 yield stable forms of sulfur compounds. Since flue gases from which sulfur dioxide is to be removed usually contain a certain amount of oxygen ($\alpha>1$), the process of sulfur removal will obviously be carried out in an oxidizing medium, leading to the formation of sulfates of the reacting metals.

The appearance of sulfites is improbable in this case, since they all are unstable compounds that in the presence of oxygen at high temperatures change into the corresponding sulfates.

The removal of sulfur dioxide from gases at high temperatures may involve the use of solid reactants containing such metals as calcium, magnesium, manganese, iron, and others. The melting and decomposition points of certain pure metals, oxides, sulfates, and carbonates [14] of these metals are given below:

	Ca	Mg	Zn	Fe	Mn
t_{melt}, °C.	850	650	1868	1539	1244
t_{vap}, °C.	1480	1105	4750	3070	2095

	CaO	MgO	ZnO	Fe_2O_3	Fe_3O_4	FeO	MnO
t_{melt}, °C.	2585	2800	2000	1565	1550	1420	1650
t_{vap}, °C.	3500	2800	—	—	—	—	—

	$CaSO_4$	$MgSO_4$	$FeSO_4$	$Fe_2(SO_4)_3$	$MnSO_4$
t_{dec}, °C.	960	1100	500	650	850
t_{melt}, °C.	1420	—	—	—	700

	$CaCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$
t_{dec}, °C.	910	680	400	300

The removal of sulfur dioxide from flue gases by means of solid reactants can in principle be carried out over a wide temperature range, from 200 to 1000°C. Considering that the flue gases contain a considerable amount of carbon dioxide, which together with sulfur dioxide may enter into reactions with the solid absorbents, in order to decrease the consumption of the reactants, the temperature of the process should be above the dissociation temperature of the carbonates of the metals employed.

The dissociation of anhydrous iron carbonate (or of the mineral siderite) is described by the following overall equation:

$$n\,FeCO_3 = m\,FeO + q\,Fe_3O_4 + p\,CO_2 + r\,CO.$$

According to the data of certain authors [36], the decomposition of iron carbonate occurs at 400°C., and at 500°C. the dissociation ends completely. The decomposition of manganese carbonate, taking place in an oxygen atmosphere according to the reaction $MnCO_3 + {}^1/_2\,O_2 = MnO_2 + CO_2$, is observed at 300°C. [37].

In a carbon dioxide atmosphere, the dissociation of $MnCO_3$ occurs in stages, $MnCO_2 \rightleftarrows MnO + CO_2$, followed by oxidation of manganous oxide according to the reaction $3MnO + CO_2 \rightarrow Mn_3O_4 + CO$ at 339-369°C.

A decomposition temperature of about 620-680°C. was determined for the dissociation of magnesium carbonate $MgCO_3 = MgO + CO_2$ [38]. A large number of studies [14] have dealt with the process of decomposition of calcium carbonate.

According to the data of many authors, the dissociation temperature of calcium carbonate fluctuates depending on its content of impurities (Table 34).

According to the data of O. A. Yesin and P. V. Gel'd [14], the metal carbonates considered above form the following series in order of stability: $MnCO_3$, $FeCO_3$, $MgCO_3$, $CaCO_3$. This is also confirmed by the temperature dependence of the dissociation pressure of carbonates (Fig. 36).

An evaluation of the above decomposition temperatures of metal carbonates shows that in order to purify the flue gases at temperatures of 500°C. and above, it is desirable to use manganese and iron oxides. A selectivity of the process with respect to sulfur dioxide is thus achieved.

At purification temperatures above 700°C., magnesium oxide can be used additionally. Above 900°C., calcium oxides can be used in addition to the indicated metal oxides.

In order to obtain a preliminary estimate of the feasibility of reactions between the indicated metal oxides and sulfur dioxide, the thermodynamic

Table 34

Content of Impurities in Calcium Carbonate (in %)

Carbonate	$CaCO_3$	$MgCO_3$	R_2O_3	$FeCO_3$	Insoluble Residue	Decomposition Temperature, °C
Calcite	99,17	0,67	0,07	—	0,05	910
Chalk	97,18	0,42	0,17	0,34	0,79	914
Marble	96,41	2,90	0,04	—	0,22	921
Limestone	90,51	2,32	2,40	0,94	2,87	900

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equilibrium of these reactions was analyzed. Table 35 gives the values of calculated free energies (ΔZ/T) of the individual reactions. As is evident from this table, for all the metal oxides discussed (Ca, Mg, Fe, Mn), one can observe a sufficient thermodynamic probability of occurrence of reactions between these oxides and sulfur dioxide in the presence of oxygen at 300-1000°C. Some thermodynamic limitations on the maximum temperature in such a process exist for iron oxides (not above 600°C.) and manganese oxides (not above 900°C.).

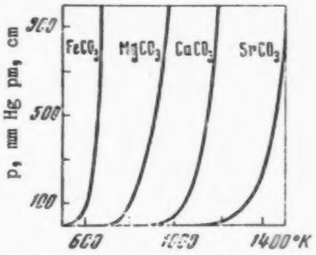

Fig. 36. Temperature dependence of the dissociation pressure of carbonates.

Considering the temperatures which are technologically permissible when metal oxides are used, i.e., the fusion and dissociation temperatures of metal oxides and sulfates, one can reach the following conclusions: when iron oxides are employed, it is desirable to carry out the process of removal of sulfur dioxide from gases at temperatures up to 400°C; when manganese oxides are employed, the temperature of the process should not exceed 800°C.; calcium and magnesium oxides can be used in processes of gas removal at temperatures up to 1000°C.

In setting up a technological process of removal of sulfur dioxide from flue gases under actual conditions, the preparation of the necessary metal oxides should obviously be based on the use of natural raw material in the form of minerals: limestone, chalk, magnesite, dolomite, siderite, and others. Thus, it is of practical interest to determine the thermodynamic characteristics of the reaction between sulfur dioxide and carbonates of the

Table 35

Free Energies of Reactions of Sulfur Dioxide with Metal Oxides.

Reaction	$\Delta Z/T$ at Temperature, °C.							
	300	400	500	600	700	800	900	1000
$CaO + SO_2 + 0{,}5\,O_2 \rightleftarrows CaSO_4$	−141,27	−110,38	−87,58	−70,10	−56,29	−48,57	−36,04	−28,44
$MgO + SO_2 + 0{,}5\,O_2 \rightleftarrows MgSO_4$	−201,73	−161,52	−131,65	−108,56	−90,13	−77,94	−62,60	−52,0[illegible]
$ZnO + SO_2 + 0{,}5\,O_2 \rightleftarrows ZnSO_4$	−76,41	−56,12	−41,20	−29,82	−20,88	−15,22	−7,84	−2,96
$Fe_2O_3 + 2SO_2 + 0{,}5\,O_2 \rightleftarrows 2\,FeSO_4$	−69,03	−41,82	−21,37	−5,35	+7,62	+16,33	+27,51	+35,39
$Fe_3O_4 + 3SO_2 + O_2 \leftrightarrows 3\,FeSO_4$	−134,08	−85,91	−49,67	−21,24	+1,81	+17,35	+37,25	+51,33
$FeO + SO_2 + 0{,}5\,O_2 \rightleftarrows FeSO_4$	−79,36	−56,77	−39,93	−26,87	−16,40	−9,56	−0,68	+5,41
$Fe + SO_2 + O_2 \rightleftarrows FeSO_4$	−173,60	−134,65	−105,70	−83,32	−65,45	−53,89	−38,76	−28,40
$MnO_2 + SO_2 \rightleftarrows MnSO_4$	—	—	−34,78	−26,84	−20,59	−15,59	−11,49	−8,10
$2\,Mn_2O_3 + SO_2 \leftrightarrows MnSO_4 + Mn_3O_4$	—	—	−19,62	−12,91	−7,62	−3,38	+0,09	+2,98
$Mn_3O_4 + 3\,SO_2 + O_2 \rightleftarrows 3\,MnSO_4$	—	—	−98,95	−70,94	−48,77	−30,83	−16,15	−3,77
$MnO + SO_2 + 0{,}5\,O_2 \rightleftarrows MnSO_4$	—	—	−47,71	34,56	−24,15	−17,59	−8,86	−3,09

Table 36

Free Energies of Reactions of Sulfur Dioxide with Metal Carbonates

Reaction	$\Delta Z/T$ at Temperature, °C.							
	300	400	500	600	700	800	900	1000
$CaCO_3 + SO_2 + 0{,}5\,O_2 = CaSO_4 + CO_2$	−107,44	−88,07	−73,91	−63,14	−54,72	−49,56	−42,58	−38,10
$MgCO_3 + SO_2 + 0{,}5\,O_2 = MgSO_4 + CO_2$	−96,48	−78,57	−65,10	−54,41	−46,02	−40,28	−32,97	−27,84
$ZnCO_3 + SO_2 + 0{,}5\,O_2 = ZnSO_4 + CO_2$	−88,20	−71,99	−59,93	−50,57	−43,04	−38,12	−31,65	−27,18
$FeCO_3 + SO_2 + 0{,}5\,O_2 = FeSO_4 + CO_2$	−155,63	−118,48	−105,57	−95,43	−87,18	−81,61	−74,42	−69,34
$MnCO_3 + SO_2 + 0{,}5\,O_2 = MnSO_4 + CO_2$	−80,93	−62,65	−48,52	−37,10	−27,56	−20,65	−12,20	−5,79

metals considered in the presence of oxygen. Table 36 gives calculated values of the free energies of these reactions at different temperatures.

The table shows that the removal of sulfur dioxide from gases is thermodynamically feasible in the presence of oxygen by means of carbonates of calcium, magnesium, iron, zinc and manganese over a wide temperature range, from 300 to 1000°C. This range covers temperatures exceeding the dissociation temperature of the carbonates considered. Hence, actually above these dissociation temperatures, the laws governing the reactions between sulfur dioxide and oxides of these metals, not their carbonates, are applicable. Below the dissociation temperatures of carbonates, the direction of the reactions toward the formation of metal sulfates instead of their carbonates is determined by the effect of the joint presence of sulfur dioxide and salts of weak acids.

Thus, a thermodynamic evaluation of the reaction of oxides and carbonates of several metals (Ca, Mg, Fe, Mn, Zn) with sulfur dioxide in an oxidizing medium indicates the probability of their occurrence at high temperatures, which provides a basis for the development of suitable technological processes of sulfur removal from flue gases.

In this connection, in order to ensure the necessary technical-economic effectiveness of such processes, it is necessary to consider the problems of utilization of the recovered sulfur, i.e., the conditions of processing of the metal sulfates formed, with the obtaining of commercial products.

A practical solution to the problem of utilization of recovered sulfur with simultaneous regeneration of the original absorbents can be the thermal decomposition of metal sulfates by roasting. In this case one can obtain sulfur dioxide with a concentration in the gaseous phase that is acceptable for industrial use (up to 10%). Without touching on the technological and technical-economic evaluation of such a solution, one should note that the temperature conditions of the process of thermal decomposition of sulfates will be different for different metals.

The thermal decomposition of iron sulfate should be carried out at temperatures above 500-600°C., that of manganese sulfate above 700°C., and that of magnesium sulfate, above 1000-1100°C. Higher temperatures are required by the roasting of $CaSO_4$. The choice of optimum temperatures for the roasting process should be made in each specific case by taking into account the possibilities of ensuring suitable economic indices of the entire process of removal of sulfur dioxide from the gases.

EVALUATION OF THE ACTIVITY OF SOLID REACTANTS IN THE COURSE OF REMOVAL OF SULFUR DIOXIDE FROM GASES AT HIGH TEMPERATURES*

Analysis of the thermodynamic studies shows that a high temperature process of removal of sulfur dioxide from flue gases is possible and should be carried out by using oxides and carbonates of calcium, magnesium, iron and manganese over a wide temperature interval, from 200 to 1000°.

Calcium and magnesium oxides, whose sulfates decompose at temperatures above 1100°C., are the most acceptable reactants in the removal of sulfur dioxide from gases. Thus, it is necessary to determine the activity of oxides of these metals in their reaction with sulfur dioxide and when the latter is mixed with oxygen at 1100°C. The studies were carried out on a unit with continuous recording of the rate of the process, as indicated by the volume of the escaping gas. The procedure was the same as in experiments involving the removal of hydrogen sulfide from gases described earlier.

The initial reactants used were chemically pure calcium oxide, magnesium oxide, their mixtures, and kaolin with a particle size of 0.25-0.5 mm. The calcium and magnesium oxides were first pressed into pellets using a hydraulic press (pressure of 1.5 T/cm^2), then broken down to the necessary particle size.

Pure sulfur dioxide was used in the experiments. As a result it was found (Fig. 37) that the highest activity toward pure sulfur dioxide at 1100°C., a linear gas velocity of 0.11 cm/sec and a contact time of 7.1 sec is displayed by calcium oxide, followed by a mixture of calcium oxide and magnesium oxide, kaolin, and pure magnesium oxide. To evaluate the role of oxygen in the process, experiments were also carried out using a mixture of sulfur dioxide and oxygen. The volume concentration of sulfur dioxide was 65.3, that of oxygen 7.3, and that of nitrogen, 27.4%. The linear velocity of the gaseous mixture was 0.157 cm/sec, and the contact time, 4.45 sec. A considerable decrease in the activity of the metal oxides used was found in the reaction with sulfur dioxide (Fig. 38).

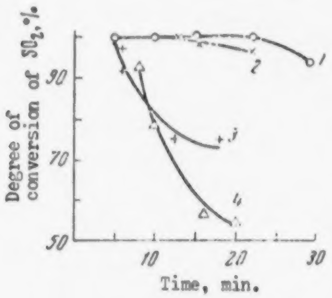

Fig. 37. Reaction of pure sulfur dioxide with metal oxides at 1100°C. (v = 0.11 cm/sec, τ = 7.1 sec)

1 - CaO; 2 - CaO + MgO; 3 - kaolin; 4 - MgO.

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*The study of SO_2 removal from flue gases by various ores, particularly limestone and manganese ore, was conducted in collaboration with A. Z. Yurovskiy, T. I. Sendul'skaya, M. Ya. Shpirt, and V. L. Gershkovich.

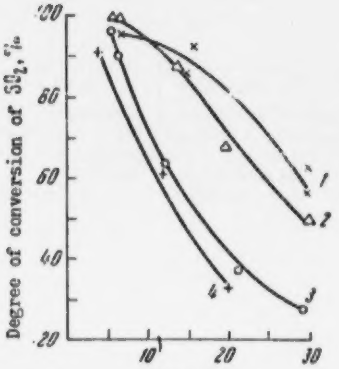

Fig. 38. Reaction of sulfur dioxide with metal oxides in an oxidizing medium (temperature 1100°C., $v = 0.157$ cm/sec, $\tau = 4.45$ sec)

1 - CaO + MgO; 2 - CaO; 3 - MgO; 4 - kaolin

The highest value is reached by the degree of conversion of sulfur dioxide during the first 4-6 min of the reaction (90-96%), after which it falls off sharply for all the reactants studied.

The highest activity in the oxidizing medium was found in the case of the mixture of calcium and magnesium oxides, followed by calcium oxide, magnesium oxide, and kaolin. In the experiments performed, the decrease in the activity of the reaction of metal oxides was due not only to a decrease in the concentration of sulfur dioxide in the gaseous mixture as a result of the addition of oxygen, but also to a slight increase in the linear velocity and hence, a decrease in contact time. A study of the composition of the gaseous phase showed that almost all of the oxygen is consumed in the formation of metal sulfates, which were observed in the solid residue.

The study of the activity of the solid reactants showed the fundamental feasibility of the process of removal of sulfur dioxide from flue gases by means of calcium and magnesium oxides and their mixtures at 1100°C.

The use of not only oxides of calcium and magnesium but also those of other metals and their carbonates for the removal of sulfur dioxide from gases is determined by the technological considerations of the process and in the first place by the temperature conditions. In the experimental determination of the activity of other metals in processes of desulfurization of flue gases, use was made of natural ores and minerals, which were selected by taking into account their availability for practical use. The reactants used were limestone, magnesite, siderite (of the Bakal deposit), KMA hematite, magnetite, manganite, pyrolusite of the Nikopol' deposit, and sphalerite (roasted). A comparative study of the reactivity of these solid reactants was conducted at 700°C. The linear velocity of the gas supplied was 0.5 m/sec, the contact time, 0.19 sec, the layer height, 95-100 mm, and the particle size, 0.5-1.0 mm.

The study involved the use of a gaseous mixture in a cylinder at a pressure of 100 atm, close in composition to the flue gases and having the following volume concentration (in %): SO_2 0.44, CO_2 12.05, O_2 5.25, N_2 82.26.

Most active with respect to sulfur dioxide at 700°C. were dolomite and calcium oxide, which was obtained by roasting natural limestone (for four hours at 1000°C.) (Fig. 39).

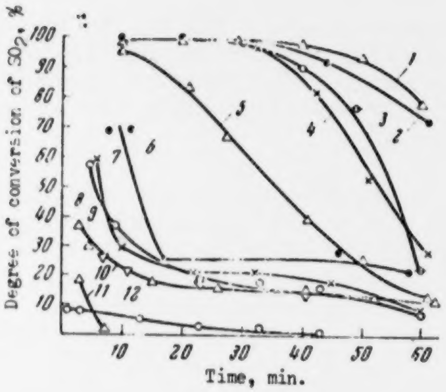

Fig. 39. Reaction of sulfur dioxide with solid reactants at 700°C. ($v = 0.5$ m/sec, $\tau = 0.19$ sec).

1 - unroasted dolomite; 2 - roasted limestone; 3 - unroasted limestone; 4 - manganite; 5 - pyrolusite; 6 - magnesite; 7 - hematite; 8 - magnetite; 9 - siderite; 10 - roasted sphalerite; 11 - sphene; 12 - chromite

When dolomite is used for 40 min, a degree of purification of the flue gas equal to 98% is obtained; during the next 20 min, a decrease in the degree of purification to 78.18% is observed. The degree of purification of the gas with calcium oxide (roasted $CaCO_3$) amounts to 99.23% in the course of the first 32 min, and during the next 60 min decreases to 72%. Natural limestone also possesses a high reactivity during the first 30 min of the reaction, when the purification is 98.45%, after which it decreases to 89.11% in 40 min and to 22.33% in 60 min.

Comparison of the activity of natural limestone and limestone preroasted to calcium oxide shows that, other conditions being equal, the removal of sulfur dioxide from flue gas is achieved in the course of a longer period of time when roasted limestone is used. This is apparently due to the presence of carbon dioxide in the flue gas.

It is probable that when natural limestone is used to purify the flue gas, the carbon dioxide present in the latter effects a decrease in the degree of purification toward the end of the reaction period, shifting the reaction equilibrium to the opposite side, whereas during the purification with calcium oxide, the same carbon dioxide leads to the formation of calcium carbonate and has a lesser effect on the gas purification.

Next in activity in their reaction with sulfur dioxide are manganite and pyrolusite of the Nikopol' deposit.

The removal of sulfur dioxide from the flue gas by manganite amounts to 96-99% during 32.5 min, then decreases to 52.44% during the following 51 min. Pyrolusite is much less active than manganite. For pyrolusite, a 96% purification takes place only during 10 min, then decreases to 66.75% during 27.5 min.

In the reaction with hydrogen sulfide, pyrolusite is more active than manganite. This is due to the chemical composition of these ores. Natural manganite $MnO_2Mn(OH)_2$ has the following chemical composition (in %): MnO 40.4; MnO_2 49.4; H_2O 10.2, and small amounts of SiO_2, Fe_2O_3 and other impurities. Pyrolusite contains chiefly MnO_2, which accounts for 63.2% of Mn, and the impurities Fe_2O_3, SiO_2, H_2O. Obviously, the presence of manganous oxide in manganite is more readily oxidized by sulfur dioxide than the high oxidized form, i.e., pyrolusite MnO_2.

As was shown by experiments using other reactants, the lowest reactivity is displayed by roasted magnesite, KMA hematite, magnetite, siderite (of the Bakal deposit), roasted sphalerite, chromite, and sphene. As far as the use of iron ores for the removal of sulfur dioxide from flue gases is concerned, the degree of purification with hematite and magnetite during the first 5-6 min of the reaction amounts to only 57.9-59%.

The removal of sulfur dioxide from the gas by iron ores was carried out at 700°C., above the temperature of thermal decomposition of iron sulfate. The use of iron oxides for desulfurization of flue gases should be carried out at up to 400°C., when the iron sulfate formed is stable.

Thus, the completed series of experiments aimed at determining the activity of natural ores toward sulfur dioxide showed that in the removal of sulfur compounds from flue gases at 700°C., the following solid reactants can be used: dolomite, limestone, and manganese ore - manganite and pyrolusite.

The possibility of using these ores is also confirmed by thermodynamic analysis of the reactions between sulfur dioxide and the chief elements entering into the composition of these ores.

REMOVAL OF SULFUR DIOXIDE FROM GASES BY CALCIUM OXIDE

Considering the great reactivity of calcium oxide toward sulfur dioxide, it is expedient to make a more detailed study of the physicochemical conditions of purification of flue gases by natural limestone. First of all, it was necessary to elucidate the effect of the blast velocity on the rate of sulfur removal from flue gases, the effect of the temperature of the process, and effect of particle size. Particular attention was given to the result of binding of sulfur in the solid residue, for the purpose of evaluating the conditions of regeneration of the absorbent so that it can be used further in the process of purification of flue gases.

The study of the optimum conditions of recovery of sulfur dioxide from flue gases was conducted in the same manner as the study of removal of hydrogen sulfide from gases on an installation described earlier. Before the experiment, the limestone used was roasted for 5 hr at 1000°C. The unreacted sulfur dioxide was determined by passing the gas through an aqueous solution of iodine and by quantitative evaluation of the results according to the reaction

$$SO_2 + J_2 + 2H_2O = H_2SO_4 + 2HJ.$$

Experiments designed to study the effect of the feed velocity of the gaseous mixture on the rate of removal of sulfur dioxide from the flue gas were conducted at 700°C. The linear velocity of the gas supplied was varied from 0.32 to 1.78 m/sec. The composition of the gas (in %) approximated that of the flue gas: SO_2 0.5; CO_2 14.4; O_2 4.0 and N_2 81.1. The size of the absorbent granules was 0.5-1.0 mm. As the blast rate was raised from 0.32 to 1.78 m/sec, the rate of the reaction of sulfur dioxide with calcium oxide increased during the first 10 min. The degree of conversion for this period of purification of the flue gas was 98-99%. After 15 min, the rate of the reaction of sulfur dioxide with calcium oxide decreased sharply as the blast velocity sharply decreased. This is apparently because at high blast velocities (1.17 and 1.78 m/sec), a large amount of reactant is consumed, and the layer height and contact time decrease to values that are not conducive to a high degree of gas purification. In addition, the degree of conversion of sulfur dioxide at lower gas supply velocities, 0.32-0.43 m/sec, was 97-99% for 40 min (Fig. 40). Such a degree of conversion of sulfur dioxide at a blast velocity of 0.85 m/sec was observed for 20 min, and at a blast velocity of 1.17 m/sec, for only 10 min. At a blast velocity of 1.78 m/sec, the degree of conversion falls to 82.77% in 10 min. Under the conditions studied, it was not possible to exclude the effect of the feed velocity of the gaseous mixture on the rate of the main process of purification. In this case, the degree of purification is also substantially affected by the rate of supply of the reacting gaseous mixture to the surface of the reactant. Nevertheless, the completed series of experiments clearly show that the removal of sulfur dioxide from the flue gas (98-99%) in the course of 40 min can be carried out at a linear velocity of 0.32-0.43 m/sec and a contact time of 0.22-0.24 sec. The degree of utilization of the solid reactant in the experiments reached as high as 22%. However, such a degree of utilization did not fully characterize the performance of the absorbent, since the duration of the experiment did not exceed 1 hr. Subsequently, the reactant was able to purify the flue gas, and thus its degree of utilization may be considerably increased under actual conditions.

The study of the effect of temperature on the removal of sulfur dioxide from flue gas by calcium oxide was conducted both in a medium of pure sulfur dioxide and in a gaseous medium similar to flue gas in composition.

The study of the effect of temperature during the reaction of calcium oxide with pure sulfur dioxide was conducted at 310, 570 and 1100°C. at a linear gas velocity of 0.11 cm/sec and a contact time of 7.1 sec (without considering the temperature).

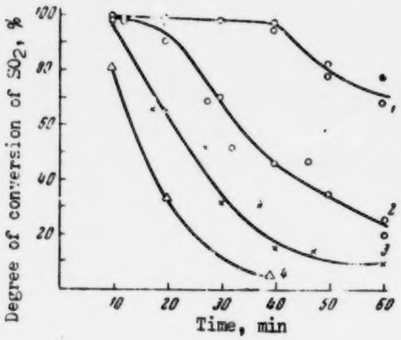

Fig. 40. Change in the degree of conversion of SO_2 with time for the reaction $SO_2 + CaO$ at different blast velocities (temperature 700°C., SO_2 concentration 0.5%).

1 - v_1 = 0.41 m/sec, τ_1 = 0.23 sec; 2 - v_2 = 0.85 m/sec, τ_2 = 0.11 sec; 3 - v_3 = 1.17 m/sec, τ_3 = 0.08 sec; 4 - v_4 = 1.78 m/sec, τ_4 = 0.053 sec.

The highest value of the degree of conversion of sulfur dioxide was reached at 1100°C., 99.5-100% in the course of 25 min of the reaction (Fig. 41). Such a degree of conversion of sulfur dioxide at 310 and 570°C. is observed only during the first 5 min of the experiment. During the subsequent periods, the degree of conversion decreases.

The effect of temperature on the rate of purification of the flue gas by roasted limestone was studied at 500, 600, 700 and 800°C. The linear velocity of the gas was 0.41 m/sec, and the contact time, 0.21 sec. The concentration of sulfur dioxide in the gaseous mixture was 0.5; CO_2 14.4; O_2 4.0; N_2 81.1%.

The degree of conversion of sulfur dioxide at 800°C. was 97.27-98.81% in the course of 60 min (Fig. 42). At 700°C., the increased degree of conversion of sulfur dioxide, 95-99%, is preserved up to 40 min of the reaction, then crops to 67.84%, and at 600°C. during 10 min amounts to 88.35% and in the course of 1 hr decreases to 47.05%. A low degree of purification of the flue gases is observed at 500°C., this being due to the formation of the carbonate salt. As the temperature is raised to 700-800°C., while the rate of formation of the carbonate salts decreases because the dissociation temperature is approached (900°C.), the removal of sulfur dioxide is more complete, but during a longer period of time.

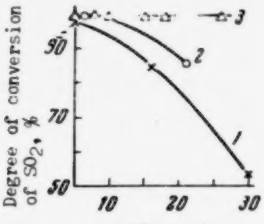

Fig. 41. Change in the degree of conversion of pure sulfur dioxide reacting with calcium oxide at different temperatures.

1 - 310°C.; 2 - 570°C.; 3 - 1100°C.

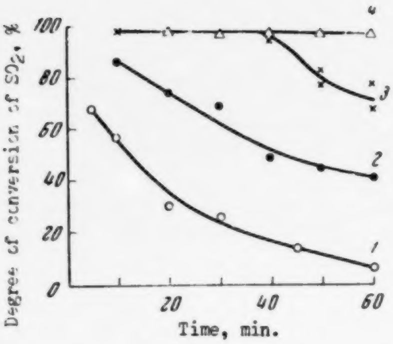

Fig. 42. Change in the degree of conversion of sulfur dioxide in the flue gas in the reaction with CaO (SO_2 0.5%, v = 0.41 m/sec, τ = 0.23 sec) at different temperatures.

1 - 500°C.; 2 - 600°C.; 3 - 700°C.; 4 - 800°C.

The study performed showed the practical feasibility of the process of removal of sulfur dioxide from flue gases by calcium oxide at high temperatures, 600-800°C. Of major importance is the evaluation of the solid residue for the purpose of regenerating calcium oxide and utilizing the recovered sulfur.

To determine the phase composition of the wolid absorbent, studies were conducted on the reaction of sulfur dioxide with limestone at different temperatures in a neutral medium of nitrogen containing 0.2-0.3% sulfur dioxide and 1.0% oxygen. The phase composition of the products of the reaction of limestone with sulfur dioxide at different temperatures is shown in Table 37.

Table 37

Phase Composition

SO_2 content, vol. %	Temperature, °C	Content of Sulfur Compounds in the Solid Phase, wt. %.		
		$CaSO_4$	$CaSO_3$	CaS
0,20	500	—	63	37
0,35	600	—	31	69
0,26	700	32	19	49
0,25	800	89	6	5
0,21	900	94	4	2

It is evident from the table that up to 700°C., the bulk of the sulfur is recovered in the form of calcium sulfite and sulfide. As the temperature is raised, the amount of these salts of sulfur compounds decreases markedly.

The phase analysis of products of the reactions between sulfur dioxide and limestone depends greatly on the oxygen content of the flue gases. For the usual oxygen content of flue gases, 3-7%, and a temperature above 600°C., chiefly calcium sulfate is formed in the solid residue, and the total amount

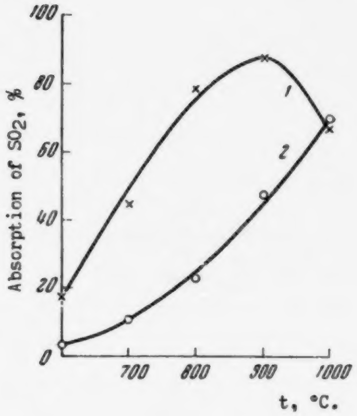

Fig. 43. Absorption of SO_2 by calcium carbonate at different temperatures.

1 - chalk (0.4-1.6 mm fraction); 2 - limestone (0.4-1.6 mm fraction).

of sulfide and sulfite does not exceed 2-4% of the amount of sulfate. The recovery of sulfur dioxide from calcium sulfate requires roasting at 1400-1500°C., which can hardly be justified. The problems of regeneration of the absorbents in this process require further study. Of practical interest is the evaluation of the degree of utilization of the reactants at different temperatures in the course of removal of sulfur from flue gases by natural limestone and chalk.

Gas of the following composition was used in the experiments (in %): SO_2 0.3-0.4; CO_2 7.9; O_2 6.55; N_2 85.25. The results of the experiments are presented in Table 38. It is evident from the latter that the reaction of natural limestone with sulfur dioxide begins practically at 700°C. and takes place most completely at 900 and 1000°C. The temperature of the start of the reaction of chalk with sulfur dioxide is slightly lower, about 600°C. Chalk is more reactive at reaction temperatures up to 900°C. (Fig. 43). The high reactivity of chalk as compared with that of limestone is explained by its large internal surface area.

At 1000°C., the process of absorption of sulfur dioxide takes place at the same rate on limestone and chalk. The degree of conversion of sulfur dioxide is substantially determined by the particle size of the absorbent and increases as the particle size decreases from 3 to 1.6 mm (see Table 38).

As the temperature rises, the degree of utilization of the reactant increases. For chalk, it rises from 13 to 49% in the 600-900°C. range. For limestone, it increases from 3.15 to 35% under the same conditions.

The above study leads to the conclusion that in the removal of sulfur dioxide from flue gases, chalk can be used side by side with limestone. For these solid reactants as well as for roasted limestone, effective solutions should be found for the problems of utilization of the recovered sulfur and repeated use of absorbents in the process.

Table 38

Results of Recovery of Sulfur Dioxide with Limestone and Chalk.

Temperature, °C.	SO_2, %	S_{tot}, in Solid Sorbent, %	Degree of Absorption, %	Linear Velocity, m/sec	Contact time, sec	Utilization of Sorbent, %
Limestone, 1.6-0.4 mm fraction						
600	0,390	0,73	4,35	1,28	0,039	3,15
700	0,390	1,85	11,10	1,44	0,035	7,90
800	0,390	3,86	23,00	1,58	0,032	16,70
900	0,390	9,40	48,50	1,72	0,029	35,00
1000	0,390	13,34	70,00	1,93	0,026	51,00
Chalk, 1.6-0.4 mm fraction						
600	0,390	3,12	19,00	1,28	0,039	13,20
700	0,390	7,17	45,00	1,44	0,035	32,50
800	0,300	10,66	85,00	1,58	0,032	47,50
900	0,300	12,55	88,00	1,72	0,029	49,00
1000	0,300	10,55	63,00	1,83	0,027	37,50
Chalk, 2.5-1.6 mm fraction						
600	0,290	4,05	17,30	1,18	0,042	17,20
700	0,294	11,87	52,10	1,38	0,038	52,00
800	0,315	14,56	62,00	1,34	0,037	62,00
Limestone, 3-1.6 mm fraction						
600	0,270	2,04	8,60	1,27	0,039	8,60
700	0,300	4,60	15,00	1,28	0,039	19,60
800	0,345	5,58	18,20	1,23	0,041	18,20
900	0,263	8,51	26,60	1,75	0,028	26,50
1000	0,348	4,50	17,00	1,42	0,035	17,00
Limestone, 1.6-0.5 mm fraction						
600	0,275	1,78	8,80	1,25	0,040	7,60
900	0,240	9,16	30,90	1,81	0,028	31,00
1000	0,313	13,27	47,50	1,56	0,032	47,00

Note. For the 1.6-0.4 mm fraction, the duration of the experiment was taken as 60 min, and for the 2.5-1.6. 3-1.6 and 1.6-0.5 mm fractions, 120 min.

REMOVAL OF SULFUR DIOXIDE FROM FLUE GASES BY MANGANESE OXIDES

The activity of manganite in the reaction of sulfur dioxide with solid natural materials is noteworthy. Thermodynamic analysis has shown that in an oxidizing medium, manganese sulfate is formed in the solid residue during the reduction of sulfur dioxide. From the standpoint of the conditions of regeneration of the absorbent, manganese sulfate may prove to be a more useful reactant, since it decomposes at temperatures up to 1000°C., evolving sulfur dioxide into the gaseous phase.

In our experimental studies, the purification material used for desulfurizing the flue gases was natural manganite of the Nikopol' deposit, $MnO_2Mn(OH)_2$. Its chemical composition is MnO 40.4; MnO_2 49.4; H_2O 10.2%, and small amounts of SiO_2, Fe_2O_3, and other impurities. The composition of the gas supplied was as follows (in %): SO_2 0.44; CO_2 3.3; O_2 14.4; N_2 81.86.

The experiments were conducted at 700°C., with a layer height of 150 mm, a particle size of 0.5-1.0 mm, and linear gas velocities of 0.43, 0.53 and 0.93 m/sec.

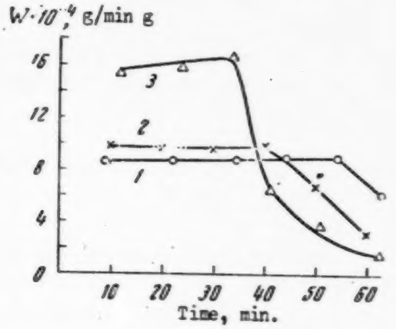

Fig. 44. Change in the rate of reaction of sulfur dioxide with manganite at different gas flow rates at 700°C.

1 - v_1 = 0.43 m/sec, τ_1 = 0.31 sec; 2 - v_2 = = 0.58 m/sec, τ_2 = 0.29 sec; 3 - v_3 = 0.93 m/sec, τ_3 = 0.16 sec.

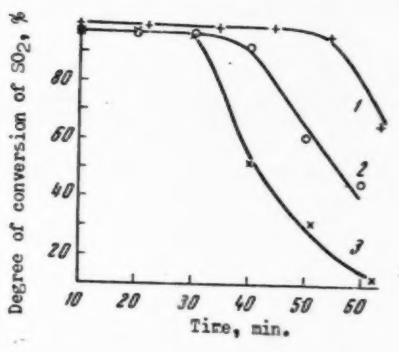

Fig. 45. Change in the degree of conversion of sulfur dioxide in the reaction with manganite with time at different gas flow rates (designation of curves same as in Fig. 44).

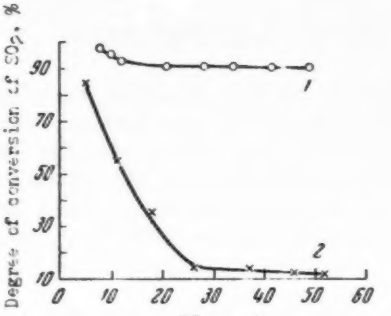

Fig. 46. Change in the degree of conversion of sulfur dioxide in the reaction with manganite with time at different gas flow rates (SO_2 = 1.92%).

1 - v_1 = 0.48 m/sec, τ_1 = 0.20 sec; 2 - v_2 = = 1.79 m/sec, τ_2 = 0.092 sec.

An increase in the feed velocity of the gaseous mixture led to an increase in the reaction rate and a decrease in the degree of removal of sulfur dioxide from the flue gas (Fig. 44). For a gas feed velocity of 0.43 m/sec, its degree of purification was 95-99.65% during 54 min (Fig. 45), and at 0.93 m/sec, a 96% conversion of sulfur dioxide was observed in the course of 34 min. For comparison, experiments were carried out with a gas having a higher concentration of sulfur dioxide, 1.92%, at blast velocities of 0.48 and 1.72 m/sec (Fig. 46). Increasing the feed velocity of the gas being purified also led to an increase in the reaction rate of sulfur dioxide with manganese oxides during the first 5-8 min of the experiment, and then, at a higher blast velocity, 1.79 m/sec, it dropped sharply. As the blast velocity increased, the degree of purification of the gas decreased, owing to a decrease in the time of contact of the gas with particles of the solid absorbent.

The degree of consumption of the solid reactant at the lower blast velocity was 44.7%, and at a velocity of 1.79 m/sec, 33.4%.

A study of the effect of temperature on the rate of removal of sulfur dioxide from the gases was conducted at 500, 600 and 700°C. with the following gas composition (in %): SO_2 0.41; O_2 14.4; N_2 81.89, a linear gas velocity of 0.42 m/sec and a contact time of 0.3 sec.

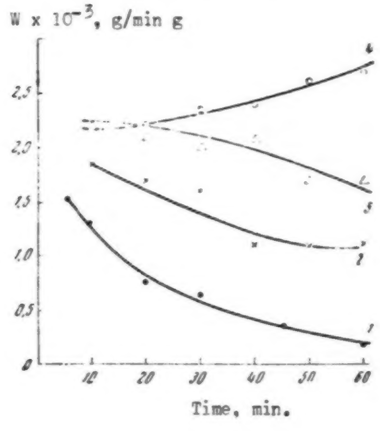

Fig. 47. Change in the rate of the reaction of sulfur dioxide with manganite with time at different temperatures.

1 - 500°C.; 2 - 600°C.; 3 - 700°C.; 4 - 800°C.

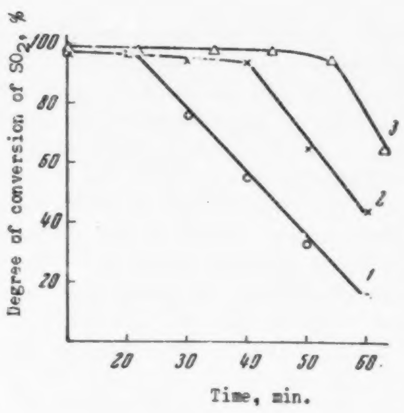

Fig. 48. Change in the degree of conversion of sulfur dioxide in the reaction with manganite with time at different temperatures.
1 - 500°C.; 2 - 600°C.; 3 - 700°C.

As the temperature rose from 500 to 700°C., the purification rate of the gas increased (Fig. 47). The highest degree of conversion of sulfur dioxide was observed at 700°C. and reached 96-99.65% in the course of 54 min (Fig. 48). As the gas purification temperature was lowered, the degree of conversion decreased slightly. At 500°C., a 98% degree of conversion of sulfur dioxide lasts only during the first 20 min of the experiment.

A study of the reaction of sulfur dioxide with natural manganite at different temperatures showed that the purification of flue gases may be achieved at 500-700°C. with a sufficient degree of removal. In addition, the purification of the flue gas involved the use of other grades of manganese ore of the Nikopol' deposit, in particular, ore of the Grushevskiy quarry (A) and concentrate (B), the chemical composition of which is given below:

Component, %	A	Б	Component, %	A	Б
Mn	29,90	44,70	MgO	1,98	1,00
MnO_2	18,60	50,60	Na_2O	—	0,44
SO_2	24,50	16,10	K_2O	—	1,19
Al_2O_3	4,40	1,80	P	0,23	0,22
Fe_2O_3	3,80	2,10	S	—	0,21
CaO	4,38	1,50	CO_2	—	0,21

The flue gas being purified had the following composition (in %): SO_2 0.74-0.86; CO_2 12.3; O_2 4.5; N_2 82.34-82.46. The degree of conversion of sulfur dioxide in the reaction with natural ore of the Grushevskiy quarry was slightly higher than in the reaction with the concentrate. Apparently, the degree of conversion is substantially affected by calcium and magnesium oxides.

A definitive utilization of the indicated natural manganese ores requires further study of the characteristics of the physicochemical reaction.

Analysis of the solid phase during the reaction of sulfur dioxide with manganese ore showed that the content of sulfide sulfur is negligibly low (0.014-0.06%), all the sulfur from the gas being bound as sulfate sulfur. In order to obtain a preliminary evaluation of the possibilities of repeated use of the reactant, after the cycle of absorption of sulfur dioxide by manganite, thermal decomposition of manganese sulfate was carried out at 900-1000°C. in a stream of air in the course of 2 hr. The total sulfur content was determined in the solid material. The absorptive capacity of manganite decreased somewhat after a quintuple absorption of sulfur dioxide. This is explained by the fact that in the thermal decomposition of manganese sulfate, the sulfur absorbed is not completely evolved. Up to 50% of the recovered sulfur remained in the solid phase, causing a decrease in the degree of removal of sulfur dioxide from the gas in a later cycle. In order to increase the rate of thermal decomposition of manganese sulfate, it is necessary to raise the roasting temperature.

Another variant of the process of regeneration of the solid absorbent may be the low-temper method of dissolution of manganese sulfate in water followed by separation of the manganese sulfate solution.

The experiments performed showed the fundamental possibility of setting up the process of purification of flue gases with the aid of natural manganese ore at 500-700°C. The problems of regeneration and repeated use of the reactants should be investigated further in order to determine the optimum characteristics of the process as a whole.

III

USE OF HIGH-TEMPERATURE REMOVAL OF SULFUR COMPOUNDS FROM GASES IN LAYOUTS OF THERMAL ELECTRIC POWER PLANTS

As was noted earlier, at the present time, in connection with the development of high-temperature technology and the widespread use of sulfur fuel and sulfur-containing raw material, a solution must be found to the problem of high-temperature removal of hydrogen sulfide and sulfur dioxide from gases. This is required both from the standpoint of purely technological considerations and for the purpose of sanitary protection of the purity of the air reservoir.

In recent years, this problem has acquired a particular importance in modern thermal-power engineering, where it is necessary to apply an effective solution to the problem of utilization of sulfur mazuts and coals by major thermal electric power plants.

A survey of the state of development of this problem revealed a very scant number of studies dealing with high-temperature removal of hydrogen sulfide and sulfur dioxide from gases. In the case of hydrogen sulfide removal from gases, this involves the process of sulfur removal at 300-400°C. by means of iron oxides, and in the case of sulfur dioxide removal, the process using manganese oxides. Promising results in reducing the sulfur content of flue gases have been obtained by blowing limestone and dolomite into the gas stream directly into the high-temperature zones of the boiler unit. At lower temperatures (up to 200°C.), the investigators' attention was concentrated on the development of sulfur removal processes based on the use of activated carbon.

A substantial number of studies and experimental industrial work have been conducted on the so-called liquid (wet) processes of sulfur removal, which are carried out at temperatures not above 100°C. Liquid processes of hydrogen sulfide removal from gases have found extensive applications in the chemical, gas, petrochemical and other industries. As far as liquid processes of removal of sulfur dioxide from gases are concerned, despite their adequate technical foundation, they are not used for the purification of gases with a low SO_2 content, particularly in the case of sulfur removal from flue gases, because of unsatisfactory technical-economic indices.

Considering the clearly inadequate amount of study devoted to problems of hydrogen sulfide and sulfur dioxide from gases at temperatures that can be practically employed, i.e., around 400-1000°C., the authors carried out numerous theoretical and experimental studies with the aim of at least partially filling this gap.

The results of these studies, presented in the preceding chapters, permit one to draw the sufficiently definite conclusion that the required high-temperature processes of removal of hydrogen sulfide or sulfur dioxide from gaseous mixtures are feasible. In addition, the completed studies provide a basis for a preliminary determination of the prospects and for the formulation of general views regarding the applicability of high-temperature processes of sulfur removal at thermal electric power plants using sulfur-containing types of fuels (mazut, coal).

The process of high-temperature removal of hydrogen sulfide from gases may find applications at thermal electric power plants in the preparation of sulfur fuel for combustion through its preliminary gasification. In this case, noxious discharges of ash and sulfur compounds into the atmosphere are absent. At the same time, the reliability of the operation of boiler units increases as a result of elimination of abrasive wear by ash and of the effect of sulfuric acid corrosion. A special importance is assumed by a reliable operation of modern power units as their unit capacity increases. It has been calculated, for example, that the total loss involved in incomplete stoppage of a power unit of 200,000 kW capacity amounts to several tens of thousands of rubles.

When gasification of solid fuel is included as a stage of its preparation for combustion at thermal electric power plants, one can exclude the equipment of units for pulverizing the fuel and also electric precipitators for removing fly ash from the flue gases and the installation for the removal of sulfur compounds.

Since the combustion will not involve a solid fuel, but the power-producing gas obtained from it, one can increase the thermal stress of the furnaces and heating surfaces by a factor of approximately 2, and hence, decrease the outside dimensions of the boiler unit.

For the conditions of high-capacity thermal electric power plants, the gasification of fuels should be expediently carried out under pressure, and this will permit a considerable improvement of the technical-economic indices of this process and will facilitate the creation of high-capacity units corresponding to the scale of utilization of the fuel at the electric power plants. If the high-pressure gas obtained must be used in furnaces at atmospheric pressure, the potential energy of the compressed purified gas will be used in an expansion gas turbine. This turbine actuates an air compressor which compresses that part of the air which is removed for gasification from the total amount of air supplied for the combustion of fuel (~40%). A flow diagram of such a thermal power plant is shown in Fig. 49.

On the basis of gasification under pressure, the problem of utilization of sulfur mazuts and low-quality solid fuels is being effectively solved in new power installations of high-capacity thermal electric power plants, more economical than steam turbine installations. In the USSR and elsewhere, major work is being carried out for the purpose of creating electric power plants with steam-gas and gas-turbine installations where the fuel is burned in furnaces under pressure, so that their thermal stress can be increased, the layout simplified, the reliability increased, and the main indices of the production of electric power improved.

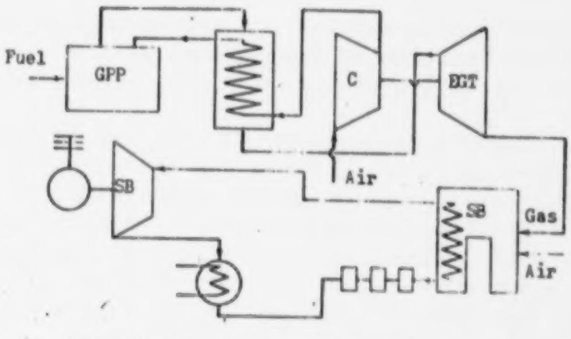

Fig. 49. Flow diagram of steam-turbine electric power plant with preliminary gasification of fuels.
GPP - gas-producer plant; C - air compressor; EGT - expansion gas turbine; SB - steam boiler; ST - steam turbine.

According to the data of the TsKTI im. I. I. Polzunov (Central Scientific Research Institute for Boilers and Turbines) [39], the introduction of the steam-gas installations developed by this institute in place of steam turbine installations of equal capacity and of the same steam parameters in gas-mazut electric power plants can provide the following savings (in %): in fuel, 7-15; in specific metal consumption, up to 28; in specific capital investments, up to 25; in labor expended on construction and assembly work, up to 30; in cost of electric power, up to 15. An even greater effect resulting from the introduction of steam-gas installations is found by comparing these indices of the installations with thermal steam-turbine electric power plants operating on solid fuel. The technical-economic indices of steam-turbine plants operating on solid fuel are known to be less favorable than those of analogous plants operating on gas.

Steam-gas and gas-turbine electric power plants set high requirements on the purity of the working substances and therefore on the types of fuel utilized. The most convenient fuel from this standpoint are combustible gases. More serious difficulties are involved in the use of mazuts, particularly sulfur mazuts, because of the corrosion of the vanes, turbines, air heaters and other parts of the unit. Despite numerous studies along these lines, no solutions have been found thus far to the problem of direct utilization of solid fuel in these installations.

The most realistic solution to this problem consists in the preliminary gasification of sulfur mazuts and solid fuels, involving the use of the purified gas obtained in the new power installations. Figures 50 and 51 show schematic diagrams of steam-gas and gas-turbine installations using purified power-producing gas obtained from gasification of the fuel. A diagram of the operation of a gas turbine with discharge of the flue gases into the boiler and use of gasification of the fuels is shown in Fig. 52.

Thus, in modern steam-turbine and new steam-gas and gas-turbine electric power plants, the gasification of sulfur fuel should be regarded as an important preliminary stage of its preparation for combustion.

Objectives arise in connection with the creation of new processes of gasification of low-quality solid fuels and sulfur mazuts satisfying the requirements of thermal-power engineering with regard to the total energy efficiency and a sufficient intensity of the process, i.e., a rate that would permit the creation of high-output gas producers. These objectives have been worked on for several years at the laboratory of gas processes of the Institute of Mineral Fuels, and this has resulted in the proposal of new methods of gasification of sulfur mazuts and solid fuels [42].

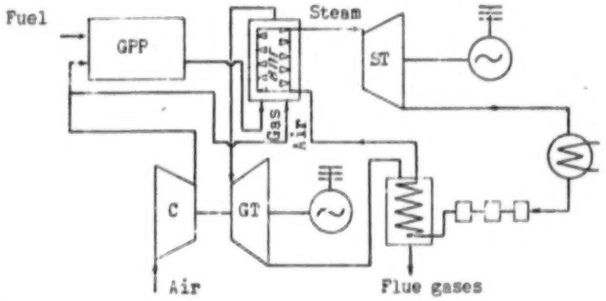

Fig. 50. Diagram of steam-gas electric power plant with preliminary gasification of fuels.
GT - gas turbine; ST - steam turbine; C - air compressor; GPP - gas-producer plant.

A characteristic feature of these methods is the removal of soot, fly ash and sulfur compounds from the gases at 1000-1100°C., which permits one to increase the total energy efficiency of production of the gas to 94-96% on mazut and 92-93% on solid fuel. The high-temperature removal of soot and dust from gases is achieved by combining cyclones (coarse purification) with granular and ceramic filters (fine purification). In addition, steps have been developed that permit a maximum reduction of the formation and entrainment of soot and dust (use of water-mazut emulsions of catalysts, high pressures). The removal of sulfur compounds (hydrogen sulfide) from gases at high temperatures is accomplished by means of solid reactants consisting of alkaline earth oxides of metals. The dissociation temperatures of carbonates of these metals are below the temperature of the gas purification process (900-1000°C.), and their sulfides are thermally stable and characterized by a high melting point. The perfected methods of gasification of sulfur mazuts and low-quality solid fuels are characterized by a high intensity of the main gasification process. Under laboratory conditions, during the gasification of sulfur mazuts, the thermal stress of the reaction volume of the gas generator reached 35 x 10^6 kcal/m^3 hr, or 8000 kg/m^2 hr. During the gasification of fine-grained brown coals (0-10 mm) in a fluidized bed at a pressure of 20 t atm, a generator-shaft cross-sectional stress of 10,000-12,000 kg/m^2 hr is reached.

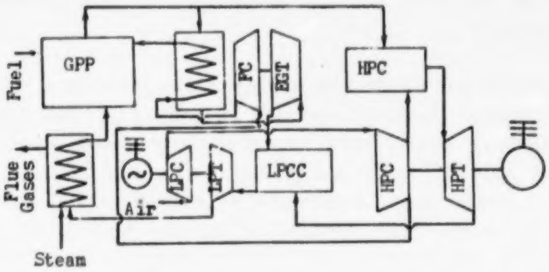

Fig. 51. Diagram of gas-turbine electric power plant with preliminary gasification of fuels.
FC - final air compressor; GPP - gas-producer plant; HPCC - high-pressure combustion chamber; HPC - high-pressure air compressor; HPT - high-pressure gas turbine; LPC - low-pressure air compressor; LPCC - low-pressure combustion chamber; LPT - low-pressure gas turbine.

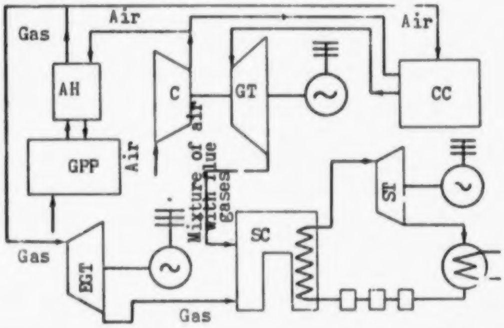

Fig. 52. Diagram of gas-turbine electric power plant with discharge into boiler.
CC - combustion chamber; AH - air heater;
EGT - expansion gas turbine; SB - steam boiler; remaining designations same as in Figs. 50 and 51.

It is not necessary to emphasize that the use of gasification of fuels as a preliminary stage of their preparation for combustion can be technically and economically justified only by ensuring a high total energy efficiency of the process. For this reason, the use for this purpose of the process of high-temperature removal of hydrogen sulfide from gases, which in contrast to other processes makes it possible to conduct the purification without appreciable heat loss, is a decisive factor in achieving the necessary indices.

A technological flow diagram of the gasification of sulfur mazuts according to the method of the Institute of Mineral Fuels is shown in Fig. 53. The gasification is carried out with a pure air blast using aqueous emulsions of sulfur mazuts consisting of a monodisperse system in which water in the form of minute droplets is dispersed throughout the mazut (water - mazut).

It was established experimentally that the use of a water-mazut emulsion creates favorable conditions for atomizing the fuel in the reaction volume, thus ensuring a uniformity of the process with a minimum formation of soot. The hot gas obtained during the gasification, with a temperature of about 1100°C., undergoes high-temperature purification involving the removal of soot in a cyclone and in a multilayered heat-stable granular filter. The layout of a granular soot-removing apparatus specifies the possibility of changing the filter and its regeneration, followed by the return of the particle layer into the soot remover. After the purification, the gas at a temperature of about 1000-1100°C. is led into the sulfur remover, which contains a layer of calcium oxide particles, obtained by firing natural limestone. The gas freed from sulfur compounds enters the energy user at a temperature of 900-1000°C. After the sulfur removal, the solid reactant, which consists of a mixture of calcium sulfide with unreacted calcium oxide, is subjected to regeneration by firing in a separate unity. The regeneration gases, containing about 10% SO_2, are used for the production of sulfuric acid or elemental sulfur. In some cases, it is possible also to use a solid reactant after the sulfur remover for the production of structural materials. In experiments on the gasification of heavy sulfur mazuts under a pressure of 20 g atm at a high intensity of the process (up to 8000 kg/m^2 hr for mazut), a gas with a caloric value of 1100-1150 kcal/m^3 was obtained. The yield of dry gas per 1 kg of anhydrous mazut was 5.75-5.9 m^3/kg, and the utilization of air was 4.3-4.4 m^3/kg of mazut. The average composition of the purified gas obtained was (in %): CO_2 8-9; CO 15-16; H_2 12-13; CH_4 2.5-3.3; N_2 60.

The flow scheme of gasification of solid fuels by the method of the Institute of Mineral Fuels differs from that of sulfur mazuts only in the process by which the hot unpurified gas is obtained. In this case, the gasification of coals is carried out in a fluidized bed of fine-grained particles at 900-1100°C. and a pressure of 20 g atm. When the processes are carried out in a fluidized bed under pressure, this permits the elimination of the drawbacks characterizing the most modern processes of gasification: the intensity of the process is increased, the outside dimensions of the gas producer and other equipment are decreased, and the entrainment of solid material is reduced. The hot gas obtained from the solid fuel in gas producers with a fluidized bed under pressure is subjected to the removal of dust and hydrogen sulfide at high temperatures in accordance with a flow scheme analogous to that of purification of the hot gas from mazuts. In experiments on the gasification of brown coals (W^P = 25%) in a fluidized bed at a pressure of 20 t atm with a steam-air blast, a gas with a thermal conductivity of 1150 kcal/m^3 was

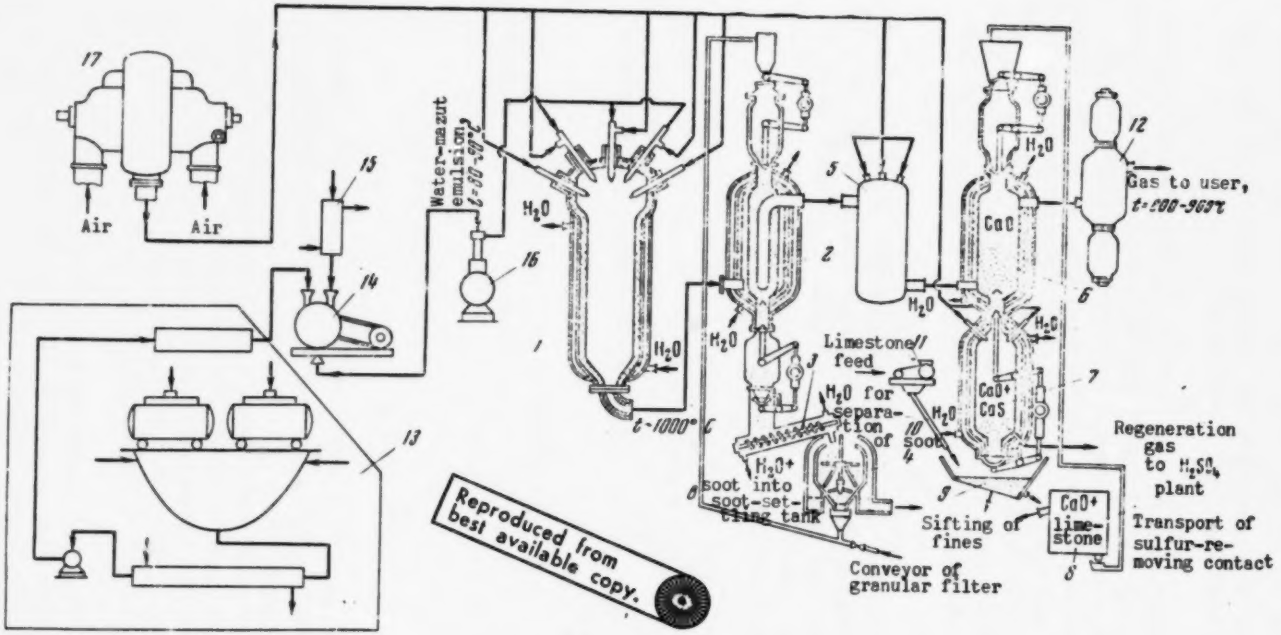
17
Air
Air
15
14
13
Water-mazut emulsion, t=80-90°C
16
H₂O
H₂O
1
t~1000°C
2
3
H₂O
H₂O+ soot into soot-settling tank
Limestone feed
11
H₂O for separation of soot
10
4
5
H₂O
CaO
H₂O
6
H₂O
CaO+ CaS
7
9
Sifting of fines
CaO+ limestone
8
12
Gas to user, t=800-960°C
Regeneration gas to H₂SO₄ plant
Transport of sulfur-removing contact
Conveyor of granular filter

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Fig. 53. Diagram of gasification of sulfur mazuts under pressure with high-temperature removal of soot and sulfur compounds from the gas.

1 - gas producer; 2 - soot catcher with high-temperature granular filter; 3 - screw washer of granular filter for removal of soot; 4 - centrifuge; 5 - gas heater; 6 - sulfur remover with high-temperature sulfur-removing contact; 7 - regenerator of sulfur removing contact; 8 - intermediate container [capacity] for sulfur-removing contact; 9 - screen; 10 - limestone conveyor; 11 - screw limestone grinder; 12 - dust catcher; 13 - unit for preparation of mazut according to the scheme of the All-Union State Planning Institute; 14 - mazut emulsifier of the Khotuntsev-Pushkin system; 15 - water heater; 16 - pump for water-mazut emulsion; 17 - blast turbocompressor.

obtained with approximately the following composition (in %): CO_2 9-10; CO 18-20; H_2 11-13; CH_4 2-2.5; N_2 54-55. For 1 m^3 of the gas obtained, the utilization of air was 0.7 m^3, and that of steam, 0.06-0.10 kg. The yield of the gas per 1 kg of working fuel was 3.0 m^3.

A technical-economic evaluation of the perfected methods of gasification of sulfur mazuts and low-quality solid fuels showed their high efficiency in the national economy. At the present time, there are sufficient technical and technical-economic prerequisites for the development of a high-intensity gasification of solid fuels and sulfur mazut with a high-temperature purification of the gases as the preliminary step of their preparation for combustion at high-capacity electric power plants. This also provides a rational solution to the problem of sanitary protection of the atmosphere around thermal electric power plants.

Considering the evaluation of the prospects for the use of high-temperature removal of sulfur dioxide from flue gases, one should note that the studies performed showed only the feasibility of such a process with the aid of certain metal oxides (CaO, MnO_2). However, no adequate solution has been found for the problems of utilization of the sulfur and regeneration of the absorbents used.

In order to achieve favorable economic indices of the process of flue gas purification, it is necessary to envisage combining the production of electric power with that of commercial chemicals by using the recovered sulfur and the absorbents themselves.

An effective solution of these problems will create favorable conditions for the use of the process of high-temperature removal of sulfur dioxide from flue gases at thermal electric power plants.

CONCLUSION

At the present time, in the USSR and throughout the world, the problem of recovery of sulfur compounds (H_2S and SO_2) from industrial gases is assuming a particular urgency, chiefly from the standpoint of sanitary protection of the air reservoir. Of no less importance is the possibility of utilizing the sulfur recovered from the gases, since the demand for it is rising steadily. An examination of the technical publications dealing with this problem shows that the solution has consisted primarily in the creation of low-temperature, liquid processes of sulfur removal from gases.

However, new, highly effective technological processes in power engineering, metallurgy, chemistry and other branches of technology are based on the use of high temperatures. Their realization depends largely on the feasibility of using the purification of heated gaseous mixtures by removing the sulfur compounds (H_2S and SO_2) which they contain without lowering the temperature.

No studies have been made thus far on the creation of high-temperature processes of sulfur removal from gases. This made it necessary to set up a series of theoretical and experimental studies in order to find effective conditions for the removal of hydrogen sulfide and sulfur dioxide from gases at high temperatures. First, studies were made on the problems of selection of solid reactants suitable for removing hydrogen sulfide from gases at 500-1100°C. and sulfur dioxide at 400-800°C. These reactants should be thermally stable and after reacting should yield stable forms of sulfur compounds. When natural substances containing these reactants are used, their dissociation temperatures should be below the temperature of the main process of sulfur removal in order to prevent the formation of carbonates in the case of purification of sulfur gases containing carbon dioxide.

The suitability and practical expediency of using calcium, iron and magnesium oxides present in such inexpensive natural minerals and ores as limestone, hematite, magnetite, siderite, pyrolusite, manganese concentrates of various grades, and others, for the removal of hydrogen sulfide from gases was experimentally demonstrated.

Limestone, dolomite, pyrolusite and manganite can be used for the removal of sulfur dioxide from gases at high temperatures.

The conditions of sulfur removal from gases by use of selected reactants were further studied in detail, as well as the problems of their regeneration with the extraction of the recovered sulfur. Thermodynamic analysis of the reactions of hydrogen sulfide and sulfur dioxide with selected metal oxides showed that they could be carried out within the indicated temperature interval. Thermodynamically favorable conditions were also established for the regeneration of metal sulfides by oxidizing with air or by steam-air treatment with formation of solid metal oxides and gaseous sulfur products.

Numerous experiments were conducted to study the kinetics of the reactions of calcium oxide, iron oxides and manganese oxides with hydrogen sulfide, on the basis of which optimum conditions were established for the removal of sulfur from power gases at 500-1100°C.

Suitable experiments on the study of the kinetic conditions were conducted on the reactions of sulfur dioxide with calcium and manganese oxides at 400-900°C.

Experimental studies were also made on the course of the regeneration reactions of calcium, iron and manganese sulfides in connection with the repeated use of solid reactants in the sulfur-removal process.

On the whole, the studies performed make it possible to conclude that the processes of high-temperature removal of sulfur compounds from gases by means of solid reactants are entirely feasible.

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Heat Capacities ($c_p = a + bT + cT^{-2}$), Temperatures (T_1) Entropies (S), Heats of Formation ($-\Delta H$) and also Temperatures (t) and Heats of Phase Transformations (Q) of Certain Elements and Compounds.

Substance	$-\Delta H^\circ_{298}$, kcal/mole	S°_{298}, cal/deg mole	t, °C	Q, cal/mole	c_p, cal/deg mole			Temperature Interval, °K
					a	$b\cdot10^3$	$c\cdot10^{-5}$	
CO (gas)	26,40	47,30	−212	—	6,79	0,98	−0,11	298—2500
CO_2 (gas)	94,05	51,07	—	—	10,55	2,16	−2,04	298—2500
COS	33,90	55,30	—	—	11,33	2,18	−1,83	298—1800
CS_2	—	—	—	—	18,40	—	—	298— veporization temperature
CS_2	−21,00	36,20	—	—	12,45	1,60	−1,80	298—1800
Ca, α	0,0	9,95	440	270	5,31	3,33	—	298—713
Ca, β	—	—	850	2070	1,50	7,74	2,50	713—1123
Ca (liquid)	—	—	—	—	7,40	—	—	1123—1800
CaO (solid)	151,90	9,50	2600	12400	11,86	1,08	−1,66	298—2000
CaS	110,00	13,50	—	—	10,20	3,80	—	273—1000
$CaSO_4$	342,40	25,50	1193	—	16,78	23,60	—	298—1400
$CaSO_3$, α, β,	288,40	21,20	−50	48	24,98	5,24	−6,20	298—1200
Fe, α	0,0	6,49	906, 1401	326	4,18	5,92	—	298—1033
Fe, β	—	—	910	215	9,00	—	—	1033—1181
Fe, γ	—	—	1400	165	1,84	4,66	—	1181—1674
Fe, δ	—	—	1539	3670	10,50	—	—	1674—1812
Fe (liquid)	—	—	—	—	10,00	—	—	1812—3000
FeO (solid)	63,50	14,20	1371	7490	12,38	1,62	−0,38	298—1200
FeO (liquid)	—	—	—	—	16,30	—	—	1650—2000
Fe_3O_4, α	268,00	35,00	627	0	21,88	48,20	—	298—900
Fe_3O_4, β	—	—	1597	33000	48,00	—	—	900—1800
Fe_2O_3, α	197,00	21,50	677	160	23,49	18,60	−3,55	298—950
Fe_2O_3, β	—	—	777	0	36,00	—	—	950—1050
Fe_2O_3, γ	—	—	—	—	31,70	1,76	—	1050—1750
FeS, α	22,80	16,10	138	570	5,19	26,40		298—411
FeS, β	—	—	325	120	17,40	—	—	411—598
FeS, γ	—	—	1195	77,30	12,20	2,38	—	598—1468
FeS_2	42,40	12,70	190	325	17,88	1,32	−3,05	298—1000
$FeSO_4$	220,50	25,70	—	—	24,03	—	—	—
$FeCO_3$	178,70	22,20	—	—	11,03	26,80	—	298—885
H_2 (gas)	0,0	31,20	−259	—	6,52	0,78	0,12	298—3000
H_2O	68,32	16,75	0	1436	18,03	—	—	273—373
H_2O	57,80	45,13	100	9820	7,17	2,56	0,08	298—2500
H_2S	4,807	49,20	−60	—	7,02	3,68	—	298—1800

APPENDIX (Cont'd)

Substance	$-\Delta H^\circ_{298}$, kcal/mole	S°_{298}, cal/deg mole	t, °C	Q, cal/mole	c_p, cal/deg mole			Temperature Interval, °K
					a	$b \cdot 10^3$	$c \cdot 10^{-5}$	
Mg (solid)	0,0	7,77	650	2140	5,33	2,45	0,103	298—923
MgO	143,70	6,55	2770	18500	10,83	1,74	—1,48	298—2100
MgS	81,20	10,20	—	—	—	—	—	—
$MgSO_4$	305,50	21,90	1130	—	23,01	—	—	—
$MgCO_3$	262,00	15,70	—	—	18,62	13,80	—4,16	298—750
Mn,α	0,0	7,60	728	535	5,16	3,81	—	298—1000
Mn,β	—	—	1001	545	8,33	0,66	—	1000—1374
Mn,γ	—	—	1137	430	10,70	—	—	1374—1410
Mn,δ	—	—	1244	3500	11,30	—	—	1410—1517
Mn (liquid)	—	—	—	—	11,60	—	—	1517—2300
MnO	92,00	14,30	1785	13000	11,11	1,94	—0,88	298—1800
Mn_3O_4,α	331,40	35,50	1172	4970	34,64	10,82	—2,20	298—1445
Mn_3O_4,β	—	—	1560	—	50,20	—	—	1445—1800
Mn_2O_3	229,40	26,40	—	—	24,73	8,38	—3,23	298—1350
MnO_2	124,30	12,70	250	—	16,60	2,44	—3,88	298—780
MnS	49,00	18,70	1530	—	11,40	1,80	—	298—1803
MnS_2	49,50	27,30	—	—	—	—	—	—
$MnSO_4$	254,20	26,80	700	—	29,26	8,92	—7,04	298—1100
$MnCO_3$	213,90	20,50	—	—	—21,99	9,30	—4,69	298—750
O_2	0,0	49,02	—219	—	7,16	1,00	—0,40	298—3000
S (rhombic)	0,0	7,62	95,5	85	3,58	6,24	—	298—368,6
S (monoclinic)	—0,07	7,78	119	335	3,56	6,96	—	368,6—392
S (liquid)	—	—	—	—	5,40	5,50	—	392—1000
SO_2 (gas)	70,95	59,25	—76	—	10,38	2,54	—1,42	298—1800
S_2	—31,00	54,40	—	—	8,54	0,28	—0,79	298—2000
SO_3 (gas)	94,32	61,20	—	—	10,70	6,42	—3,12	298—1200
Zn (solid)	0,0	9,95	420,00	1765	5,5	2,40	—	298—692,7
Zn (liquid)	—	—	—	—	7,50	—	—	692,7—1200
ZnO	83,20	10,40	1975	—	11,71	1,22	—2,18	294—1600
ZnS	48,20	13,80	1020	—	12,16	1,24	—1,36	298—1200
ZnO_4	233,90	30,60	735	—	21,90	18,20	—	298—vaporization temperature
$ZnCO_3$	194,20	19,70	—	—	9,33	33,00	—	298—780

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